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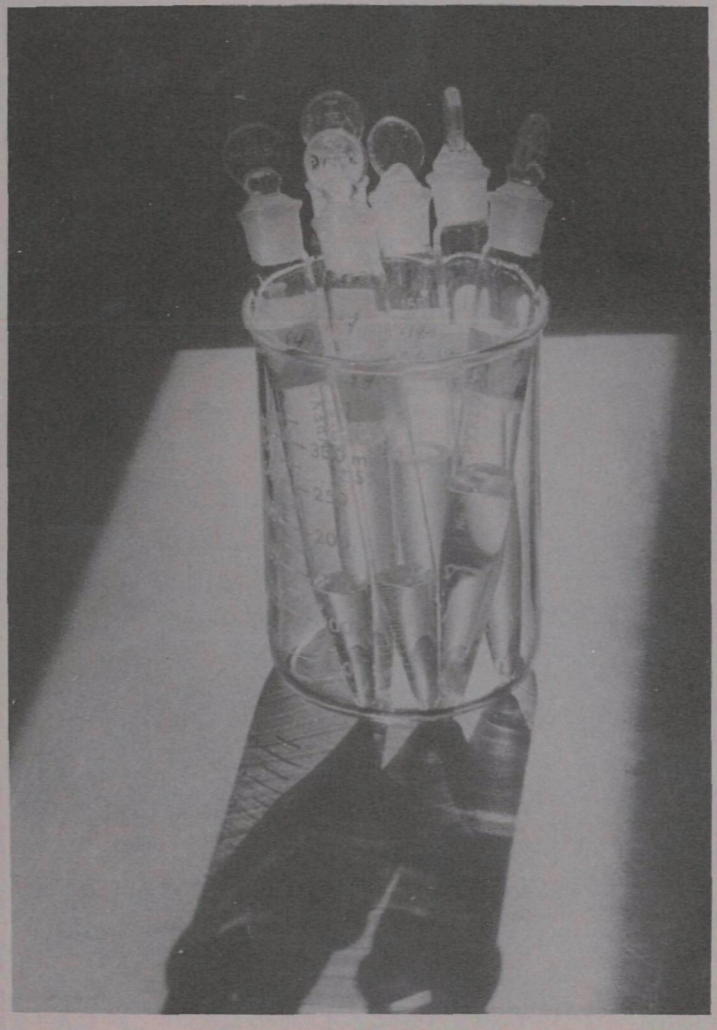
Solid Waste

Test Methods for Evaluating Solid Waste

Volume IA: Laboratory Manual Physical/Chemical Methods



VOLUME ONE,

SECTION A

Revision 0
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ABSTRACT

This manual provides test procedures which may be used to evaluate those properties of a solid waste which determine whether the waste is a hazardous waste within the definition of Section 3001 of the Resource Conservation and Recovery Act (PL 94-580). These methods are approved for obtaining data to satisfy the requirement of 40 CFR Part 261, Identification and Listing of Hazardous Waste. This manual encompasses methods for collecting representative samples of solid wastes, and for determining the reactivity, corrosivity, ignitability, and composition of the waste and the mobility of toxic species present in the waste.

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3810	Four (4.4)	5020	0
3820	Four (4.4)	None (new method)	0
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5040	Four (4.2.1)	3720	0
6010	Three	6010	0
7000	Three	7000	0
7020	Three	7020	0

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7040	Three	7040	0
7041	Three	7041	0
7060	Three	7060	0
7061	Three	7061	0
7080	Three	7080	0
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7130	Three	7130	0
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7610	Three	7610	0
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7770	Three	7770	0

Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
7840	Three	7840	0
7841	Three	7841	0
7870	Three	7870	0
7910	Three	7910	0
7911	Three	7911	0
7950	Three	7950	0
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8090	Four (4.3.1)	8090	0
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8250	Four (4.3.2)	8250	0
8270	Four (4.3.2)	8270	0
8280	Four (4.3.2)	None (new method)	0
8310	Four (4.3.3)	8310	0
9010	Five	9010	0
9020	Five	9020	0
9022	Five	9022	0
9030	Five	9030	0
9035	Five	9035	0
9036	Five	9036	0
9038	Five	9038	0
9040	Six	9040	0
9041	Six	9041	0
9045	Six	9045	0
9050	Six	9050	0

Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
9060	Five	9060	0
9065	Five	9065	0
9066	Five	9066	0
9067	Five	9067	0
9070	Five	9070	0
9071	Five	9071	0
9080	Six	9080	0
9081	Six	9081	0
9090	Six	9090	0
9095	Six	9095	0
9100	Six	9100	0
9131	Five	9131	0
9132	Five	9132	0
9200	Five	9200	0
9250	Five	9250	0
9251	Five	9251	0
9252	Five	9252	0
9310	Six	9310	0
9315	Six	9315	0
9320	Five	9320	0
HCN Test Method	Seven	HCN Test Method	0
H_2S Test Method	Seven	H_2S Test Method	0

PURPOSE OF THE MANUAL

Test Methods for Evaluating Solid Waste (SW-846) is intended to provide a unified, up-to-date source of information on sampling and analysis related to compliance with RCRA regulations. It brings together into one reference all sampling and testing methodology approved by the Office of Solid Waste for use in implementing the RCRA regulatory program. The manual provides methodology for collecting and testing representative samples of waste and other materials to be monitored. Aspects of sampling and testing covered in SW-846 include quality control, sampling plan development and implementation, analysis of inorganic and organic constituents, the estimation of intrinsic physical properties, and the appraisal of waste characteristics.

The procedures described in this manual are meant to be comprehensive and detailed, coupled with the realization that the problems encountered in sampling and analytical situations require a certain amount of flexibility. The solutions to these problems will depend, in part, on the skill, training, and experience of the analyst. For some situations, it is possible to use this manual in rote fashion. In other situations, it will require a combination of technical abilities, using the manual as guidance rather than in a step-by-step, word-by-word fashion. Although this puts an extra burden on the user, it is unavoidable because of the variety of sampling and analytical conditions found with hazardous wastes.

ORGANIZATION AND FORMAT

This manual is divided into two volumes. Volume I focuses on laboratory activities and is divided for convenience into three sections. Volume IA deals with quality control, selection of appropriate test methods, and analytical methods for metallic species. Volume IB consists of methods for organic analytes. Volume IC includes a variety of test methods for miscellaneous analytes and properties for use in evaluating the waste characteristics. Volume II deals with sample acquisition and includes quality control, sampling plan design and implementation, and field sampling methods. Included for the convenience of sampling personnel are discusssions of the ground water, land treatment, and incineration monitoring regulations.

Volume I begins with an overview of the quality control precedures to be imposed upon the sampling and analytical methods. The quality control chapter (Chapter One) and the methods chapters are interdependent. The analytical procedures cannot be used without a thorough understanding of the quality control requirements and the means to implement them. This understanding can be achieved only be reviewing Chapter One and the analytical methods together. It is expected that individual laboratories, using SW-846 as the reference

source, will select appropriate methods and develop a standard operating procedure (SOP) to be followed by the laboratory. The SOP should incorporate the pertinent information from this manual adopted to the specific needs and circumstances of the individual laboratory as well as to the materials to be evaluated.

The method selection chapter (Chapter Two) presents a comprehensive discussion of the application of these methods to various matrices in the determination of groups of analytes or specific analytes. It aids the chemist in constructing the correct analytical method from the array of procedures which may cover the matrix/analyte/concentration combination of interests. The section discusses the objective of the testing program and its relationship to the choice of an analytical method. Flow charts are presented along with tables to guide in the selection of the correct analytical procedures to form the appropriate method.

The analytical methods are separated into distinct procedures describing specific, independent analytical operations. These include extraction, digestion, cleanup, and determination. This format allows linking of the various steps in the analysis according to: the type of sample (e.g., water, soil, sludge, still bottom); analytes(s) of interest; needed sensitivity; and available analytical instrumentation. The chapters describing Miscellaneous Test Methods and Properties, however, give complete methods which are not amenable to such segmentation to form discrete procedures.

The introductory material at the beginning of each section containing analytical procedures presents information on sample handling and preservation, safety, and sample preparation.

Part II of Volume I (Chapters Seven and Eight) describes the characteristics of a waste. Sections following the regulatory descriptions contain the methods used to determine if the waste is hazardous because it exhibits a particular characteristic.

Volume II gives background information on statistical and nonstatistical aspects of sampling. It also presents practical sampling techniques appropriate for situations presenting a variety of physical conditions.

A discussion of the regulatory requirements with respect to several monitoring categories is also given in this volume. These include ground water monitoring, land treatment, and incineration. The purpose of this guidance is to orient the user to the objective of the analysis, and to assist in developing data quality objectives, sampling plans, and laboratory SOP's.

Significant interferences, or other problems, may be encountered with certain samples. In these situations, the analyst is advised to contact the Chief, Methods Section (WH-562B) Technical Assessment Branch, Office of Solid Waste, US EPA, Washington, DC 20460 (202-382-4761) for assistance. The manual is intended to serve all those with a need to evaluate solid waste. Your comments, corrections, suggestions, and questions concerning any material contained in, or omitted from, this manual will be gratefully appreciated. Please direct your comments to the above address.

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PART I METHODS FOR ANALYTES AND PROPERTIES

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CHAPTER ONE

QUALITY CONTROL

1.1 INTRODUCTION

Appropriate use of data generated under the great range of analytical conditions encountered in RCRA analyses requires reliance on the quality control practices incorporated into the methods and procedures. The Environmental Protection Agency generally requires using approved methods for sampling and analysis operations fulfilling regulatory requirements, but the mere approval of these methods does not guarantee adequate results. Inaccuracies can result from many causes, including unanticipated matrix effects, equipment malfunctions, and operator error. Therefore, the quality control component of each method is indispensable.

The data acquired from quality control procedures are used to estimate and evaluate the information content of analytical data and to determine the necessity or the effect of corrective action procedures. The means used to estimate information content include precision, accuracy, detection limit, and other quantifiable and qualitative indicators.

1.1.1 Purpose of this Chapter

This chapter defines the quality control procedures and components that are mandatory in the performance of analyses, and indicates the quality control information which must be generated with the analytical data. Certain activities in an integrated program to generate quality data can be classified as management (QA) and other as functional (QC). The presentation given here is an overview of such a program.

The following sections discuss some minimum standards for QA/QC programs. The chapter is not a guide to constructing quality assurance project plans, quality control programs, or a quality assurance organization. Generators who are choosing contractors to perform sampling or analytical work, however, should make their choice only after evaluating the contractor's QA/QC program against the procedures presented in these sections. Likewise, laboratories that sample and/or analyze solid wastes should similarly evaluate their QA/QC programs.

Most of the laboratories who will use this manual also carry out testing other than that called for in SW-846. Indeed, many user laboratories have multiple mandates, including analyses of drinking water, wastewater, air and industrial hygiene samples, and process samples. These laboratories will, in most cases, already operate under an organizational structure that includes QA/QC. Regardless of the extent and history of their programs, the users of this manual should consider the development, status, and effectiveness of their QA/QC program in carrying out the testing described here.

1.1.2 Program Design

The initial step for any sampling or analytical work should be strictly to define the program goals. Once the goals have been defined, a program must be designed to meet them. QA and QC measures will be used to monitor the program and to ensure that all data generated are suitable for their intended use. The responsibility of ensuring that the QA/QC measures are properly employed must be assigned to a knowledgeable person who is not directly involved in the sampling or analysis.

One approach that has been found to provide a useful structure for a QA/QC program is the preparation of both general program plans and project-specific QA/QC plans.

The program plan for a laboratory sets up basic laboratory policies, including QA/QC, and may include standard operating procedures for specific tests. The program plan serves as an operational charter for the laboratory, defining its purposes, its organization and its operating principles. Thus, it is an orderly assemblage of management policies, objectives, principles, and general procedures describing how an agency or laboratory intends to produce data of known and accepted quality. The elements of a program plan and its preparation are described in QAMS-004/80.

Project-specific QA/QC plans differ from program plans in that specific details of a particular sampling/analysis program are addressed. For example, a program plan might state that all analyzers will be calibrated according to a specific protocol given in written standard operating procedures for the laboratory (SOP), while a project plan would state that a particular protocol will be used to calibrate the analyzer for a specific set of analyses that have been defined in the plan. The project plan draws on the program plan or its basic structure and applies this management approach to specific determinations. A given agency or laboratory would have only one quality assurance program plan, but would have a quality assurance project plan for each of its projects. The elements of a project plan and its preparation are described in QAMS/005/80 and are listed in Figure 1-1.

Some organizations may find it inconvenient or even unnecessary to prepare a new project plan for each new set of analyses, especially analytical laboratories which receive numerous batches of samples from various customers within and outside their organizations. For these organizations, it is especially important that adequate QA management structures exist and that any procedures used exist as standard operating procedures (SOP), written documents which detail an operation, analysis or action whose mechanisms are thoroughly prescribed and which is commonly accepted as the method for performing certain routine or repetitive tasks. Having copies of SW-846 and all its referenced documents in one's laboratory is not a substitute for having in-house versions of the methods written to conform to specific instrumentation, data needs, and data quality requirements.

FIGURE 1-1

ESSENTIAL ELEMENTS OF A QA PROJECT PLAN

1. Title Page
2. Table of Contents
3. Project Description
4. Project Organization and Responsibility
5. QA Objectives
6. Sampling Procedures
7. Sample Custody
8. Calibration Procedures and Frequency
9. Analytical Procedures
10. Data Reduction, Validation, and Reporting
11. Internal Quality Control Checks
12. Performance and System Audits
13. Preventive Maintenance
14. Specific Routine Procedures Used to Assess Data Precision, Accuracy, and Completeness
15. Corrective Action
16. Quality Assurance Reports to Management

1.1.3 Organization and Responsibility

As part of any measurement program, activities for the data generators, data reviewers/approvers, and data users/requestors must be clearly defined. While the specific titles of these individuals will vary among agencies and laboratories, the most basic structure will include at least one representative of each of these three types. The data generator is typically the individual who carries out the analyses at the direction of the data user/requestor or a designate within or outside the laboratory. The data reviewer/approver is responsible for ensuring that the data produced by the data generator meet agreed-upon specifications.

Responsibility for data review is sometimes assigned to a "Quality Assurance Officer" or "QA Manager." This individual has broad authority to approve or disapprove project plans, specific analyses and final reports. The QA Officer is independent from the data generation activities. In general, the QA Officer is responsible for reviewing and advising on all aspects of QA/QC, including:

Assisting the data requestor in specifying the QA/QC procedure to be used during the program;

Making on-site evaluations and submitting audit samples to assist in reviewing QA/QC procedures; and,

f problems are detected, making recommendations to the data requestor and upper corporate/institutional management to ensure that appropriate corrective actions are taken.

In programs where large and complex amounts of data are generated from both field and laboratory activities, it is helpful to designate sampling monitors, analysis monitors, and quality control/data monitors to assist in carrying out the program or project.

The sampling monitor is responsible for field activities. These include:

Determining (with the analysis monitor) appropriate sampling equipment and sample containers to minimize contamination;

Ensuring that samples are collected, preserved, and transported as specified in the workplan; and

Checking that all sample documentation (labels, field notebooks, chain-of-custody records, packing lists) is correct and transmitting that information, along with the samples, to the analytical laboratory.

The analysis monitor is responsible for laboratory activities. These include:

Training and qualifying personnel in specified laboratory QC and analytical procedures, prior to receiving samples;

Receiving samples from the field and verifying that incoming samples correspond to the packing list or chain-of-custody sheet; and

Verifying that laboratory QC and analytical procedures are being followed as specified in the workplan, reviewing sample and QC data during the course of analyses, and, if questionable data exist, determining which repeat samples or analyses are needed.

The quality control and data monitor is responsible for QC activities and data management. These include:

Maintaining records of all incoming samples, tracking those samples through subsequent processing and analysis, and, ultimately, appropriately disposing of those samples at the conclusion of the program;

Preparing quality control samples for analysis prior to and during the program;

Preparing QC and sample data for review by the analysis coordinator and the program manager; and

Preparing QC and sample data for transmission and entry into a computer data base, if appropriate.

1.1.4 Performance and Systems Audits

The QA Officer may carry out performance and/or systems audits to ensure that data of known and defensible quality are produced during a program,.

Systems audits are qualitative evaluations of all components of field and laboratory quality control measurement systems. They determine if the measurement systems are being used appropriately. The audits may be carried out before all systems are operational, during the program, or after the completion of the program. Such audits typically involve a comparison of the activities given in the QA/QC plan with those actually scheduled or performed. A special type of systems audit is the data management audit. This audit addresses only data collection and management activities.

The performance audit is a quantitative evaluation of the measurement systems of a program. It requires testing the measurement systems with samples of known composition or behavior to evaluate precision and accuracy. The performance audit is carried out by or under the auspices of the QA Officer without the knowledge of the analysts. Since this is seldom achievable, many variations are used that increase the awareness of the analyst as to the nature of the audit material.

1.1.5 Corrective Action

Corrective action procedures should be addressed in the program plan, project, or SOP. These should include the following elements:

The EPA predetermined limits for data acceptability beyond which corrective action is required;

Procedures for corrective action; and,

For each measurement system, identification of the individual responsible for initiating the corrective action and the individual responsible for approving the corrective action, if necessary.

The need for corrective action may be identified by system or performance audits or by standard QC procedures. The essential steps in the corrective action system are:

Identification and definition of the problem;

Assignment of responsibility for investigating the problem;

Investigation and determination of the cause of the problem;

Determination of a corrective action to eliminate the problem;

Assigning and accepting responsibility for implementing the corrective action;

Implementing the corrective action and evaluating its effectiveness; and

Verifying that the corrective action has eliminated the problem.

The QA Officer should ensure that these steps are taken and that the problem which led to the corrective action has been resolved.

1.1.6 QA/QC Reporting to Management

QA Project Program or Plans should provide a mechanism for periodic reporting to management (or to the data user) on the performance of the measurement system and the data quality. Minimally, these reports should include:

Periodic assessment of measurement quality indicators, i.e., data accuracy, precision and completeness;

Results of performance audits;

Results of system audits; and

Significant QA problems and recommended solutions.

The individual responsible within the organization structure for preparing the periodic reports should be identified in the organizational or management plan. The final report for each project should also include a separate QA section which summarizes data quality information contained in the periodic reports.

Other guidance on quality assurance management and organizations is available from the Agency and professional organizations such as ASTM, AOAC, APHA and FDA.

1.1.7 Quality Control Program for the Analysis of RCRA Samples

An analytical quality control program develops information which can be used to:

Evaluate the accuracy and precision of analytical data in order to establish the quality of the data;

Provide an indication of the need for corrective actions, when comparison with existing regulatory or program criteria or data trends shows that activities must be changed or monitored to a different degree; and

To determine the effect of corrective actions.

1.1.8 Definitions

ACCURACY: Accuracy means the nearness of a result or the mean ($\bar{x}$) of a set of results to the true value. Accuracy is assessed by means of reference samples and percent recoveries.

ANALYTICAL BATCH: The basic unit for analytical quality control is the analytical batch. The analytical batch is defined as samples which are analyzed together with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar composition.

BLANK: A blank is an artificial sample designed to monitor the introduction of artifacts into the process. For aqueous samples, reagent water is used as a blank matrix; however, a universal blank matrix does not exist for solid samples, and therefore, no matrix is used. The blank is taken through the appropriate steps of the process.
A reagent blank is an aliquot of analyte-free water or solvent analyzed with the analytical batch. Field blanks are aliquots of analyte-free water or solvents brought to the field in sealed containers and transported back to the

laboratory with the sample containers. Trip blanks and equipment blanks are two specific types of field blanks. Trip blanks are not opened in the field. They are a check on sample contamination originating from sample transport, shipping and from site conditions. Equipment blanks are opened in the field and the contents are poured appropriately over or through the sample collection device, collected in a sample container, and returned to the laboratory as a sample. Equipment blanks are a check on sampling device cleanliness.

CALIBRATION CHECK: Verification of the ratio of instrument response to analyte amount, a calibration check, is done by analyzing for analyte standards in an appropriate solvent. Calibration check solutions are made from a stock solution which is different from the stock used to prepare standards.

CHECK SAMPLE: A blank which has been spiked with the analyte(s) from an independent source in order to monitor the execution of the analytical method is called a check sample. The level of the spike shall be at the regulatory action level when applicable. Otherwise, the spike shall be at 5 times the estimate of the quantification limit. The matrix used shall be phase matched with the samples and well characterized: for an example, reagent grade water is appropriate for an aqueous sample.

ENVIRONMENTAL SAMPLE: An environmental sample or field sample is a representative sample of any material (aqueous, nonaqueous, or multimedia) collected from any source for which determination of composition or contamination is requested or required. For the purposes of this manual, environmental samples shall be classified as follows:

Surface Water and Ground Water;

Drinking Water -- delivered (treated or untreated) water designated as potable water;

Water/Wastewater -- raw source waters for public drinking water supplies, ground waters, municipal influents/effluents, and industrial influents/effluents;

Sludge -- municipal sludges and industrial sludges;

Waste -- aqueous and nonaqueous liquid wastes, chemical solids, contaminated soils, and industrial liquid and solid wastes.

MATRIX/SPIKE-DUPLICATE ANALYSIS: In matrix/spike duplicate analysis, predetermined quantities of stock solutions of certain analytes are added to a added to a sample matrix prior to sample extraction/digestion and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected. The relative percent difference between the samples is calculated and used to assess analytical precision. The concentration of the spike should be at the regulatory standard level or the estimated or actual method quantification limit. When the concentration of the analyte in the sample is greater than 0.1%, no spike of the analyte is necessary.

MQL: The method quantification limit (MQL) is the minimum concentration of a substance that can be measured and reported.

PRECISION: Precision means the measurement of agreement of a set of replicate results among themselves without assumption of any prior information as to the true result. Precision is assessed by means of duplicate/replicate sample analysis.

PQL: The practical quantitation limit (PQL) is the lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions.

RCRA: The Resource Conservation and Recovery Act.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonomous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REPLICATE SAMPLE: A replicate sample is a sample prepared by dividing a sample into two or more separate aliquots. Duplicate samples are considered to be two replicates.

STANDARD CURVE: A standard curve is a curve which plots concentrations of known analyte standard versus the instrument response to the analyte.

SURROGATE: Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, standards, samples and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

WATER: Reagent, analyte-free, or laboratory pure water means distilled or deionized water or Type II reagent water which is free of contaminants that may interfere with the analytical test in question.

1.2 QUALITY CONTROL

The procedures indicated below are to be performed for all analyses. Specific instructions relevant to particular analyses are given in the pertinent analytical procedures.

1.2.1 Field Quality Control

The sampling component of the Quality Assurance Project Plan (QAPP) shall include:

Reference to or incorporation of accepted sampling techniques in the sampling plan;

Procedures for documenting and justifying any field actions contrary to the QAPP;

Documentation of all pre-field activities such as equipment check-out, calibrations, and container storage and preparation;

Documentation of field measurement quality control data (quality control procedures for such measurements shall be equivalent to corresponding laboratory QC procedures);

Documentation of field activities;

Documentation of post-field activities including sample shipment and receipt, field team de-briefing and equipment check-in;

Generation of quality control samples including duplicate samples, field blanks, equipment blanks, and trip blanks; and

The use of these samples in the context of data evaluation, with details of the methods employed (including statistical methods) and of the criteria upon which the information generated will be judged.

1.2.2 Analytical Quality Control

A quality control operation or component is only useful if it can be measured or documented. The following components of analytical quality control are related to the analytical batch. The procedures described are intended to be applied to chemical analytical procedures; although the principles are applicable to radio-chemical or biological analysis, the procedures may not be directly applicable to such techniques.

All quality control data and records required by this section shall be retained by the laboratory and shall be made available to the data requestor as appropriate. The frequencies of these procedures shall be as stated below or at least once with each analytical batch.

1.2.2.1 Spikes, Blanks and Duplicates

General Requirements

These procedures shall be performed at least once with each analytical batch with a minimum of once per twenty samples.

1.2.2.1.1 Duplicate Spike

A split/spiked field sample shall be analyzed with every analytical batch or once in twenty samples, whichever is the greater frequency. Analytes stipulated by the analytical method, by applicable regulations, or by other specific requirements must be spiked into the sample. Selection of the sample to be spiked and/or split depends on the information required and the variety of conditions within a typical matrix. In some situations, requirements of the site being sampled may dictate that the sampling team select a sample to be spiked and split based on a pre-visit evaluation or the on-site inspection. This does not preclude the laboratory's spiking a sample of its own selection as well. In other situations the laboratory may select the appropriate sample. The laboratory's selection should be guided by the objective of spiking, which is to determine the extent of matrix bias or interference on analyte recovery and sample-to-sample precision. For soil/sediment samples, spiking is performed at approximately 3 ppm and, therefore, compounds in excess of this concentration in the sample may cause interferences for the determination of the spiked analytes.

1.2.2.1.2 Blanks

Each batch shall be accompanied by a reagent blank. The reagent blank shall be carried through the entire analytical procedure.

1.2.2.1.3 Field Samples/Surrogate Compounds

Every blank, standard, and environmental sample (including matrix spike/matrix duplicate samples) shall be spiked with surrogate compounds prior to purging or extraction. Surrogates shall be spiked into samples according to the appropriate analytical methods. Surrogate spike recoveries shall fall within the control limits set by the laboratory (in accordance with procedures specified in the method or within ±20%) for samples falling within the quantification limits without dilution. Dilution of samples to bring the analyte concentration into the linear range of calibration may dilute the surrogates below the quantification limit; evaluation of analytical quality then will rely on the quality control embodied in the check, spiked and duplicate spiked samples.

1.2.2.1.4 Check Sample

Each analytical batch shall contain a check sample. The analytes employed shall be a representative subset of the analytes to be determined. The concentrations of these analytes shall approach the estimated quantification limit in the matrix of the check sample. In particular, check samples for metallic analytes shall be matched to field samples in phase and in general matrix composition.

1.2.2.2 Clean-Ups

Quality control procedures described here are intended for adsorbent chromatography and back extractions applied to organic extracts. All batches of adsorbents (Florisil, alumina, silica gel, etc.) prepared for use shall be checked for analyte recovery by running the elution pattern with standards as a column check. The elution pattern shall be optimized for maximum recovery of analytes and maximum rejection of contaminants.

1.2.2.2.1 Column Check Sample

The elution pattern shall be reconfirmed with a column check of standard compounds after activating or deactivating a batch of adsorbent. These compounds shall be representative of each elution fraction. Recovery as specified in the methods is considered an acceptable column check. A result lower than specified indicates that the procedure is not acceptable or has been misapplied.

1.2.2.2.2 Column Check Sample Blank

The check blank shall be run after activating or deactivating a batch of adsorbent.

1.2.2.3 Determinations

1.2.2.3.1 Instrument Adjustment: Tuning, Alignment, etc.

Requirements and procedures are instrument- and method-specific. Analytical instrumentation shall be tuned and aligned in accordance with requirements which are specific to the instrumentation procedures employed. Individual determinative procedures shall be consulted. Criteria for initial conditions and for continuing confirmation conditions for methods within this manual are found in the appropriate procedures.

1.2.2.3.2 Calibration

Analytical instrumentation shall be calibrated in accordance with requirements which are specific to the instrumentation and procedures employed. Introductory Methods 7000 and 8000 and appropriate analytical procedures shall be consulted for criteria for initial and continuing calibration.

1.2.2.3.3 Additional QC Requirements for Inorganic Analysis

Standard curves used in the determination of inorganic analytes shall be prepared as follows:

Standard curves derived from data consisting of one reagent blank and four concentrations shall be prepared for each analyte. The response for each prepared standard shall be based upon the average of three replicate readings of each standard. The standard curve shall be used with each subsequent analysis provided that the standard curve is verified by using at least one reagent blank and one standard at a level normally encountered or expected in such samples. The response for each standard shall be based upon the average of three replicate readings of the standard. If the results of the verification are not within ±10% of the original curve, a new standard shall be prepared and analyzed. If the results of the second verification are not within ±10% of the original standard curve, a reference standard should be employed to determine if the discrepancy is with the standard or with the instrument. New standards should also be prepared on a quarterly basis at a minimum. All data used in drawing or describing the curve shall be so indicated on the curve or its description. A record shall be made of the verification.

Standard deviations and relative standard deviations shall be calculated for the percent recovery of analytes from the spiked sample duplicates and from the check samples. These values shall be established for the twenty most recent determinations in each category.

1.2.2.3.4 Additional Quality Control Requirements for Organic Analysis

The following requirements shall be applied to the analysis of samples by gas chromatography, liquid chromatography and gas chromatography/mass spectrometry.

The calibration of each instrument shall be verified at frequencies specified in the methods. A new standard curve must be prepared as specified in the methods.

The tune of each GC/MS system used for the determination of organic analytes shall be checked with 4-bromofluorobenzene (BFB) for determinations of volatiles and with decafluorotriphenylphosphine (DFTPP) for determinations of semi-volatiles. The required ion abundance criteria shall be met before determination of any analytes. If the system does not meet the required specification for one or more of the required ions, the instrument must be retuned and rechecked before proceeding with sample analysis. The tune performance check criteria must be achieved daily or for each 12 hour operating period, whichever is more frequent.

Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. Background subtraction

actions resulting in spectral distortions for the sole purpose of meeting special requirements are contrary to the objectives of Quality Assurance and are unacceptable.

For determinations by HPLC or GC, the instrument calibration shall be verified as specified in the methods.

1.2.2.3.5 Identification

Identification of all analytes must be accomplished with an authentic standard of the analyte. When authentic standards are not available, identification is tentative.

For gas chromatographic determinations of specific analytes, the relative retention time of the unknown must be compared with that of an authentic standard. For compound confirmation, a sample and standard shall be re-analyzed on a column of different selectivity to obtain a second characteristic relative retention time. Peaks must elute within daily retention time windows to be declared a tentative or confirmed identification.

For gas chromatographic/mass spectrometric determinations of specific analytes, the spectrum of the analyte should conform to a literature representation of the spectrum or to a spectrum of the authentic standard obtained after satisfactory tuning of the mass spectrometer and within the same twelve-hour working shift as the analytical spectrum. The appropriate analytical methods should be consulted for specific criteria for matching the mass spectra, relative response factors, and relative retention times to those of authentic standards.

1.2.2.3.6 Quantification

The procedures for quantification of analytes are discussed in the appropriate general procedures (7000, 8000) and the specific analytical methods.

In some situations in the course of determining metal analytes, matrix-matched calibration standards may be required. These standards shall be composed of the pure reagent, approximation of the matrix, and reagent addition of major interferents in the samples. This will be stipulated in the procedures.

Estimation of the concentration of an organic compound not contained within the calibration standard may be accomplished by comparing mass spectral response of the compound with that of an internal standard. The procedure is specified in the methods.

1.3 DETECTION LIMIT AND QUANTIFICATION LIMIT

The detection limit and quantification limit of analytes shall be evaluated by determining the noise level of response for each sample in the batch. If analyte is present, the noise level adjacent in retention time to the analyte peak may be used. For wave-length dispersive instrumentation, multiple determinations of digestates with no detectable analyte may be used to establish the noise level. The method of standard additions should then be used to determine the calibration curve using one digestate or extracted sample in which the analyte was not detected. The slope of the calibration curve, m, should be calculated using the following relations:

m = slope of calibration line

S_B = standard deviation of the average noise level

MDL = KS_B/m

For K = 3; MDL = method detection limit.

For K = 5; MQL = method quantitation limit.

1.4 DATA REPORTING

The requirement of reporting analytical results on a wet-weight or a dry-weight basis is dictated by factors such as: sample matrix; program or regulatory requirement; and objectives of the analysis.

Analytical results shall be reported with the percent moisture or percent solid content of the sample.

1.5 QUALITY CONTROL DOCUMENTATION

The following sections list the QC documentation which comprises the complete analytical package. This package should be obtained from the data generator upon request. These forms, or adaptations of these forms, shall be used by the data generator/reportor for inorganics (I), or for organics (O) or both (I/O) types of determinations.

1.5.1 Analytical Results (I/O: Form I)

Analyte concentration.

Sample weight.

Percent water (for non-aqueous samples when specified).

Final volume of extract or diluted sample.

Holding times (I: Form X).

1.5.2 Calibration (I: Form II; O: Form V, VI, VII, IX)

Calibration curve or coefficients of the linear equation which describes the calibration curve.

Correlation coefficient of the linear calibration.

Concentration/response data (or relative response data) of the calibration check standards, along with dates on which they were analytically determined.

1.5.3 Column Check (O: Form X)

Results of column chromatography check, with the chromatogram.

1.5.4 Extraction/Digestion (I/O: Form I)

Date of the extraction for each sample.

1.5.5 Surrogates (O: Form II)

Amount of surrogate spiked, and percent recovery of each surrogate.

1.5.6 Matrix/Duplicate Spikes (I: Form V, VI; O: Form III)

Amount spiked, percent recovery, and relative percent difference for each compound in the spiked samples for the analytical batch.

1.5.7 Check Sample (I: Form VII; O: Form VIII)

Amount spiked, and percent recovery of each compound spiked.

1.5.8 Blank (I: Form III; O: Form IV)

Identity and amount of each constituent.

1.5.9 Chromatograms (for organic analysis)

All chromatograms for reported results, properly labeled with:

- Sample identification
- Method identification
- Identification of retention time of analyte on the chromatograms.

1.5.10 Quantitative Chromatogram Report (O: Forms VIII, IX, X)

Retention time of analyte.

Amount injected.

Area of appropriate calculation of detection response.

Amount of analyte found.

Date and time of injection.

1.5.11 Mass Spectrum

Spectra of standards generated from authentic standards (one for each report for each compound detected).

Spectra of analytes from actual analyses.

Spectrometer identifier.

1.5.12 Metal Interference Check Sample Results (I: Form IV)

1.5.13 Detection Limit (I: Form VII; O: Form I)

Analyte detection limits with methods of estimation.

1.5.14 Results of Standard Additions (I: Form VIII)

1.5.15 Results of Serial Dilutions (I: Form IX)

1.5.16 Instrument Detection Limits (I: Form XI)

1.5.17 ICP Interelement Correction Factors and ICP Linear Ranges (when applicable) (I: Form XII, Form XIII).

1.6 REFERENCES

1. Guidelines and Specifications for Preparing Quality Assurance Program Plans, September 20, 1980, Office of Monitoring Systems and Quality Assurance, ORD, U.S. EPA, QAMS-004/80, Washington, DC 20460.

2. Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans, December 29, 1980, Office of Monitoring Systems and Quality Assurance, ORD, U.S. EPA, QAMS-005/80, Washington, DC 20460.

Date _____

COVER PAGE
INORGANIC ANALYSES DATA PACKAGE

Lab Name _____ Case No. _____

No. _____ Q.C. Report No. _____

Sample Numbers

EPA No.	Lab ID No.	EPA No.	Lab ID No.

Comments: _____

Form I

Sample No.

Date _____

INORGANIC ANALYSIS DATA SHEET

LAB NAME _____ CASE NO. _____

Lab Receipt Date _____

LAB SAMPLE ID. NO. _____ QC REPORT NO. _____

Elements Identified and Measured

Matrix: Water _____ Soil _____ Sludge _____ Other _____

ug/L or mg/kg dry weight (Circle One)

1.	Aluminum	13.	Magnesium
2.	Antimony	14.	Manganese
3.	Arsenic	15.	Mercury
4.	Barium	16.	Nickel
5.	Beryllium	17.	Potassium
6.	Cadmium	18.	Selenium
7.	Calcium	19.	Silver
8.	Chromium	20.	Sodium
9.	Cobalt	21.	Thallium
10.	Copper	22.	Vanadium
11.	Iron	23.	Zinc
12.	Lead	Precent Solids (%)	

Cyanide _____

Comments: _____

_____

_____

_____

Lab Manager _____

Revision 0
Date September 1986

Form II

Q. C. Report No. _____

INITIAL AND CONTINUING CALIBRATION VERIFICATION

LAB NAME _____ CASE NO. _____

DATE _____ UNITS: ug/L

Compound	Initial Calib.[1]			Continuing Calibration[2]					
Metals:	True Value	Found	%R	True Value	Found	%R	Found	%R	Method[4]
1. Aluminum									
2. Antimony									
3. Arsenic									
4. Barium									
5. Beryllium									
6. Cadmium									
7. Calcium									
8. Chromium									
9. Cobalt									
10. Copper									
11. Iron									
12. Lead									
13. Magnesium									
14. Manganese									
15. Mercury									
16. Nickel									
17. Potassium									
18. Selenium									
19. Silver									
20. Sodium									
21. Thallium									
22. Vanadium									
23. Zinc									
Other: _____									
Cyanide									

[1] Initial Calibration Source [2] Continuing Calibration Source _____

[4] Indicate Analytical Method Used: P - ICP; A - Flame AA; F - Furnace AA

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Form III

Q. C. Report No. _____

BLANKS

LAB NAME _____ CASE NO. _____

DATE _____ UNITS _____

Compound	Initial Calibration Blank Value	Continuing Calibration Blank Value 1	2	3	4	Preparation Blank Matrix: 1	Matrix: 2
Metals:							
1. Aluminum							
2. Antimony							
3. Arsenic							
4. Barium							
5. Beryllium							
6. Cadmium							
7. Calcium							
8. Chromium							
9. Cobalt							
10. Copper							
11. Iron							
12. Lead							
13. Magnesium							
14. Manganese							
15. Mercury							
16. Nickel							
17. Potassium							
18. Selenium							
19. Silver							
20. Sodium							
21. Thallium							
22. Vanadium							
23. Zinc							
Other:							
Cyanide							

[1] Reporting Units: aqueous, ug/L; solid mg/kg

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Form IV

Q. C. Report No. _____

ICP INTERFERENCE CHECK SAMPLE

LAB NAME _____ CASE NO. _____

Check Sample I.D. _____

DATE _____ Check Sample Source _____

Units: ug/L

Compound	Control Limits[1] Mean	Control Limits[1] Std. Dev.	True[2]	Initial Observed	Initial %R	Final Observed	Final %R
Metals:							
1. Aluminum							
2. Antimony							
3. Arsenic							
4. Barium							
5. Beryllium							
6. Cadmium							
7. Calcium							
8. Chromium							
9. Cobalt							
10. Copper							
11. Iron							
12. Lead							
13. Magnesium							
14. Manganese							
15. Mercury							
16. Nickel							
17. Potassium							
18. Selenium							
19. Silver							
20. Sodium							
21. Thallium							
22. Vanadium							
23. Zinc							
Other: _____							

1 Mean value based on n = _____.

2 True value of EPA ICP Interference Check Sample or contractor standard.

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Form V

Q. C. Report No. _____

SPIKE SAMPLE RECOVERY

LAB NAME _____ CASE NO. _____

Sample No. _____

DATE _____ Lab Sample ID No. _____

Units _____

Matrix _____

Compound	Control Limit %R	Spiked Sample Result (SSR)	Sample Result (SR)	Spiked Added (SA)	%R[1]
Metals:					
1. Aluminum					
2. Antimony					
3. Arsenic					
4. Barium					
5. Beryllium					
6. Cadmium					
7. Calcium					
8. Chromium					
9. Cobalt					
10. Copper					
11. Iron					
12. Lead					
13. Magnesium					
14. Manganese					
15. Mercury					
16. Nickel					
17. Potassium					
18. Selenium					
19. Silver					
20. Sodium					
21. Thallium					
22. Vanadium					
23. Zinc					
Other:					
Cyanide					

[1] %R = [(SSR - SR)/SA] x 100

"N" - out of control

"NR" - Not required

Comments: _____

Revision 0

Date September 1986

Form VI

Q. C. Report No. _____

DUPLICATES

LAB NAME _____ CASE NO. _____

Sample No. _____

DATE _____ Lab Sample ID No. _____

Units _____

Matrix _____

Compound	Control Limit[1]	Sample(S)	Duplicate(D)	RPD[2]
Metals:				
1. Aluminum				
2. Antimony				
3. Arsenic				
4. Barium				
5. Beryllium				
6. Cadmium				
7. Calcium				
8. Chromium				
9. Cobalt				
10. Copper				
11. Iron				
12. Lead				
13. Magnesium				
14. Manganese				
15. Mercury				
16. Nickel				
17. Potassium				
18. Selenium				
19. Silver				
20. Sodium				
21. Thallium				
22. Vanadium				
23. Zinc				
Other:				
Cyanide				

* Out of Control

[1] To be added at a later date.

[2] RPD = [|S - D|/((S + D)/2)] x 100

NC - Non calculable RPD due to value(s) less than CRDL

Form VII

Q.C. Report No. _____

INSTRUMENT DETECTION LIMITS AND

LABORATORY CONTROL SAMPLE

LAB NAME _____ CASE NO. _____ DATE _____

LCS NO. _____

Compound	Required Detection Limits (CRDL)-ug/l	Instrument Detection Limits (IDL)-ug/l		Lab Control Sample ug/L mg/kg (circle one)		
		ICP/AA ID#_____	Furnace ID#_____	True	Found	%R
Metals:						
1. Aluminum						
2. Antimony						
3. Arsenic						
4. Barium						
5. Beryllium						
6. Cadmium						
7. Calcium						
8. Chromium						
9. Cobalt						
10. Copper						
11. Iron						
12. Lead						
13. Magnesium						
14. Manganese						
15. Mercury						
16. Nickel						
17. Potassium						
18. Selenium						
19. Silver						
20. Sodium						
21. Thallium						
22. Vanadium						
23. Zinc						
Other:						
Cyanide		NR	NR			

NR - Not required

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Form VIII

Q.C. Report No. _____

STANDARD ADDITION RESULTS

LAB NAME _____ CASE NO. _____

DATE _____ UNITS: ug/L

EPA Sample #	Element	Matrix	0 ADD ABS.	1 ADD		2 ADD		3 ADD		FINAL CON.[3]	r*
				CON.	ABS[2]	CON.	ABS.[2]	CON.	ABS.[2]		

[2] CON is the concentration added, ABS. is the instrument readout in absorbance or concentration.

[3] Concentration as determined by MSA

*"r" is the correlation coefficient.

+ - correlation coefficient is outside of control window of 0.995.

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Form IX

Q. C. Report No. _____

ICP SERIAL DILUTIONS

LAB NAME _____ CASE NO. _____

Sample No. _____

DATE _____ Lab Sample ID No. _____

Units: ug/L

Matrix _____

Compound	Initial Sample Concentration(I)	Serial Dilution[1] Result(S)	% Difference[2]
Metals:			
1. Aluminum			
2. Antimony			
3. Arsenic			
4. Barium			
5. Beryllium			
6. Cadmium			
7. Calcium			
8. Chromium			
9. Cobalt			
10. Copper			
11. Iron			
12. Lead			
13. Magnesium			
14. Manganese			
15. Nickel			
16. Potassium			
17. Selenium			
18. Silver			
19. Sodium			
20. Thallium			
21. Vanadium			
22. Zinc			
Other: _____			

[1] Diluted sample concentration corrected for 1:4 dilution (see Exhibit D)

[2] Percent Difference = $\frac{|I - S|}{I} \times 100$

NR - Not Required, initial sample concentration less than 10 times IDL

NA - Not Applicable, analyte not determined by ICP

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Form X

QC Report No. _____

HOLDING TIMES

LAB NAME _____

DATE _____ CASE NO. _____

EPA Sample No.	Matrix	Date Received	Mercury Prep Date	Mercury Holding Time[1] (Days)	CN Prep Date	CN Holding Time[1] (Days)

[1]Holding time is defined as number of days between the date received and the sample preparation date.

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Form XI

INSTRUMENT DETECTION LIMITS

LAB NAME _____ DATE _____

ICP/Flame AA (Circle One) Model Number _____ Furnace AA Number _____

Element	Wavelength (nm)	IDL (ug/L)	Element	Wavelength (nm)	IDL (ug/L)
1. Aluminum			13. Magnesium		
2. Antimony			14. Manganese		
3. Arsenic			15. Mercury		
4. Barium			16. Nickel		
5. Beryllium			17. Potassium		
6. Cadmium			18. Selenium		
7. Calcium			19. Silver		
8. Chromium			20. Sodium		
9. Cobalt			21. Thallium		
10. Copper			22. Vanadium		
11. Iron			23. Zinc		
12. Lead					

Footnotes:
- Indicate the instrument for which the IDL applies with a "P" (for ICP an "A" (for Flame AA), or an "F" (for Furnace AA) behind the IDL valu
- Indicate elements commonly run with background correction (AA) with a "B" behind the analytical wavelength.
- If more than one ICP/Flame or Furnace AA is used, submit separate Forms XI-XIII for each instrument.

COMMENTS: _____

Lab Manager _____

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Date September 1986

Form XII

ICP Interelement Correction Factors

LABORATORY _____ ICP Model Number _____

DATE _____

Analyte	Analyte Wavelength (nm)	Interelement Correction Factors for Al	Ca	Fe	Mg				
1. Antimony									
2. Arsenic									
3. Barium									
4. Beryllium									
5. Cadmium									
6. Chromium									
7. Cobalt									
8. Copper									
9. Lead									
10. Manganese									
11. Mercury									
12. Nickel									
13. Potassium									
14. Selenium									
15. Silver									
16. Sodium									
17. Thallium									
18. Vanadium									
19. Zinc									

COMMENTS: _____

Lab Manager _____

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Date September 1986

Form XII

ICP Interelement Correction Factors

LABORATORY _____ ICP Model Number _____

DATE _____

Analyte	Analyte Wavelength (nm)	Interelement Correction Factors for							
1. Antimony									
2. Arsenic									
3. Barium									
4. Beryllium									
5. Cadmium									
6. Chromium									
7. Cobalt									
8. Copper									
9. Lead									
10. Manganese									
11. Mercury									
12. Nickel									
13. Potassium									
14. Selenium									
15. Silver									
16. Sodium									
17. Thallium									
18. Vanadium									
19. Zinc									

COMMENTS: _____

_____

Lab Manager _____

Revision 0
Date September 1986

Form XIII

ICP Linear Ranges

LAB NAME _____ ICP Model Number _____

DATE _____

Analyte	Integration Time (Seconds)	Concentration (ug/L)	Analyte	Integration Time (Seconds)	Concentration (ug/L)
1. Aluminum			13. Magnesium		
2. Antimony			14. Manganese		
3. Arsenic			15. Mercury		
4. Barium			16. Nickel		
5. Beryllium			17. Potassium		
6. Cadmium			18. Selenium		
7. Calcium			19. Silver		
8. Chromium			20. Sodium		
9. Cobalt			21. Thallium		
10. Copper			22. Vanadium		
11. Iron			23. Zinc		
12. Lead					

Footnotes: • Indicate elements not analyzed by ICP with the notation "NA".

COMMENTS: _____

_____

_____

_____

Lab Manager _____

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Date September 1986

Organics Analysis Data Sheet
(Page 1)

Sample Number

Laboratory Name: _____ Case No: _____

Lab Sample ID No. _____ QC Report No: _____

Sample Matrix: _____

Data Release Authorized By: _____ Date Sample Received: _____

Volatile Compounds

Date Extracted/Prepared: _____

Date Analyzed: _____

Conc/Dil Factor: _____ pH _____

Percent Moisture: (Not Decanted) _____

CAS Number		ug/l or ug/Kg (Circle One)
74-87-3	Chloromethane	
74-83-9	Bromomethane	
75-01-4	Vinyl Chloride	
75-00-3	Chloroethane	
75-09-2	Methylene Chloride	
67-64-1	Acetone	
75-15-0	Carbon Disulfide	
75-35-4	1, 1-Dichloroethene	
75-34-3	1, 1-Dichloroethane	
156-60-5	Trans-1, 2-Dichloroethene	
67-66-3	Chloroform	
107-06-2	1, 2-Dichloroethane	
78-93-3	2-Butanone	
71-55-6	1, 1, 1-Trichloroethane	
56-23-5	Carbon Tetrachloride	
108-05-4	Vinyl Acetate	
75-27-4	Bromodichloromethane	

CAS Number		ug/l or ug/Kg (Circle One)
78-87-5	1, 2-Dichloropropane	
10061-02-6	Trans-1, 3-Dichloropropene	
79-01-6	Trichloroethene	
124-48-1	Dibromochloromethane	
79-00-5	1, 1, 2-Trichloroethane	
71-43-2	Benzene	
10061-01-5	cis-1, 3-Dichloropropene	
110-75-8	2-Chloroethylvinylether	
75-25-2	Bromoform	
108-10-1	4-Methyl-2-Pentanone	
591-78-6	2-Hexanone	
127-18-4	Tetrachloroethene	
79-34-5	1, 1, 2, 2-Tetrachloroethane	
108-88-3	Toluene	
108-90-7	Chlorobenzene	
100-41-4	Ethylbenzene	
100-42-5	Styrene	
	Total Xylenes	

Data Reporting Qualifiers

For reporting results to EPA, the following results qualifiers are used. Additional flags or footnotes explaining results are encouraged. However, the definition of each flag must be explicit.

Value If the result is a value greater than or equal to the detection limit, report the value

U Indicates compound was analyzed for but not detected. Report the minimum detection limit for the sample with the U (e.g., 10U) based on necessary concentration/dilution action. (This is not necessarily the instrument detection limit.) The footnote should read U-Compound was analyzed for but not detected. The number is the minimum attainable detection limit for the sample

J Indicates an estimated value. This flag is used either when estimating a concentration for tentatively identified compounds where a 1:1 response is assumed or when the mass spectral data indicated the presence of a compound that meets the identification criteria but the result is less than the specified detection limit but greater than zero (e.g., 10J). If limit of detection is 10 µg/l and a concentration of 3 µg/l is calculated, report as 3J.

C This flag applies to pesticide parameters where the identification has been confirmed by GC/MS. Single component pesticides ≥ 10 ng/ul in the final extract should be confirmed by GC/MS

B This flag is used when the analyte is found in the blank as well as a sample. It indicates possible/probable blank contamination and warns the data user to take appropriate action

Other Other specific flags and footnotes may be required to properly define the results. If used, they must be fully described and such description attached to the data summary report

Laboratory Name: _____

Case No: _____

Sample Number

Organics Analysis Data Sheet
(Page 2)

Semivolatile Compounds

GPC Cleanup ☐Yes ☐No

Date Extracted/Prepared: _____

Separatory Funnel Extraction ☐Yes

Date Analyzed: _____

Continuous Liquid - Liquid Extraction ☐Yes

Conc/Dil Factor: _____

Percent Moisture (Decanted) _____

CAS Number		ug/l or ug/Kg (Circle One)
108-95-2	Phenol	
111-44-4	bis(-2-Chloroethyl)Ether	
95-57-8	2-Chlorophenol	
541-73-1	1, 3-Dichlorobenzene	
106-46-7	1, 4-Dichlorobenzene	
100-51-6	Benzyl Alcohol	
95-50-1	1, 2-Dichlorobenzene	
95-48-7	2-Methylphenol	
39638-32-9	bis(2-chloroisopropyl)Ether	
106-44-5	4-Methylphenol	
621-64-7	N-Nitroso-Di-n-Propylamine	
67-72-1	Hexachloroethane	
98-95-3	Nitrobenzene	
78-59-1	Isophorone	
88-75-5	2-Nitrophenol	
105-67-9	2, 4-Dimethylphenol	
65-85-0	Benzoic Acid	
111-91-1	bis(-2-Chloroethoxy)Methane	
120-83-2	2, 4-Dichlorophenol	
120-82-1	1, 2, 4-Trichlorobenzene	
91-20-3	Naphthalene	
106-47-8	4-Chloroaniline	
87-68-3	Hexachlorobutadiene	
59-50-7	4-Chloro-3-Methylphenol	
91-57-6	2-Methylnaphthalene	
77-47-4	Hexachlorocyclopentadiene	
88-06-2	2, 4, 6-Trichlorophenol	
95-95-4	2, 4, 5-Trichlorophenol	
91-58-7	2-Chloronaphthalene	
88-74-4	2-Nitroaniline	
131-11-3	Dimethyl Phthalate	
208-96-8	Acenaphthylene	
99-09-2	3-Nitroaniline	

CAS Number		ug/l or ug/Kg (Circle One)
83-32-9	Acenaphthene	
51-28-5	2, 4-Dinitrophenol	
100-02-7	4-Nitrophenol	
132-64-9	Dibenzofuran	
121-14-2	2, 4-Dinitrotoluene	
606-20-2	2, 6-Dinitrotoluene	
84-66-2	Diethylphthalate	
7005-72-3	4-Chlorophenyl-phenylether	
86-73-7	Fluorene	
100-01-6	4-Nitroaniline	
534-52-1	4, 6-Dinitro-2-Methylphenol	
86-30-6	N-Nitrosodiphenylamine (1)	
101-55-3	4-Bromophenyl-phenylether	
118-74-1	Hexachlorobenzene	
87-86-5	Pentachlorophenol	
85-01-8	Phenanthrene	
120-12-7	Anthracene	
84-74-2	Di-n-Butylphthalate	
206-44-0	Fluoranthene	
129-00-0	Pyrene	
85-68-7	Butylbenzylphthalate	
91-94-1	3, 3'-Dichlorobenzidine	
56-55-3	Benzo(a)Anthracene	
117-81-7	bis(2-Ethylhexyl)Phthalate	
218-01-9	Chrysene	
117-84-0	Di-n-Octyl Phthalate	
205-99-2	Benzo(b)Fluoranthene	
207-08-9	Benzo(k)Fluoranthene	
50-32-8	Benzo(a)Pyrene	
193-39-5	Indeno(1, 2, 3-cd)Pyrene	
53-70-3	Dibenz(a, h)Anthracene	
191-24-2	Benzo(g, h, i)Perylene	

(1)-Cannot be separated from diphenylamine

Laboratory Name: _____

Case No: _____

Sample Number

Organics Analysis Data Sheet
(Page 3)

Pesticide/PCBs

GPC Cleanup ☐Yes ☐No

Date Extracted/Prepared: _____

Separatory Funnel Extraction ☐Yes

Date Analyzed: _____

Continuous Liquid - Liquid Extraction ☐Yes

Conc/Dil Factor: _____

Percent Moisture (decanted) _____

CAS Number		ug/l or ug/Kg (Circle One)
319-84-6	Alpha-BHC	
319-85-7	Beta-BHC	
319-86-8	Delta-BHC	
58-89-9	Gamma-BHC (Lindane)	
76-44-8	Heptachlor	
309-00-2	Aldrin	
1024-57-3	Heptachlor Epoxide	
959-98-8	Endosulfan I	
60-57-1	Dieldrin	
72-55-9	4, 4'-DDE	
72-20-8	Endrin	
33213-65-9	Endosulfan II	
72-54-8	4, 4'-DDD	
1031-07-8	Endosulfan Sulfate	
50-29-3	4, 4'-DDT	
72-43-5	Methoxychlor	
53494-70-5	Endrin Ketone	
57-74-9	Chlordane	
8001-35-2	Toxaphene	
12674-11-2	Aroclor-1016	
11104-28-2	Aroclor-1221	
11141-16-5	Aroclor-1232	
53469-21-9	Aroclor-1242	
12672-29-6	Aroclor-1248	
11097-69-1	Aroclor-1254	
11096-82-5	Aroclor-1260	

V_i = Volume of extract injected (ul)

V_s = Volume of water extracted (ml)

W_s = Weight of sample extracted (g)

V_t = Volume of total extract (ul)

V_s _____ or W_s _____ V_t _____ V_i _____

Laboratory Name: _____

Case No: _____

Sample Number

Organics Analysis Data Sheet

CAS Number	Compound Name	Fraction	RT or Scan Number	Estimated Concentration (ug/l or ug/kg)
1.				
2.				
3.				
4.				
5.				
6.				
7.				
8.				
9.				
10.				
11.				
12.				
13.				
14.				
15.				
16.				
17.				
18.				
19.				
20.				
21.				
22.				
23.				
24.				
25.				
26.				
27.				
28.				
29.				
30.				

WATER SURROGATE PERCENT RECOVERY SUMMARY

Case No. _____ **Laboratory Name** _____

	VOLATILE			SEMI-VOLATILE								PESTICIDE
SAMPLE NO.	TOLUENE-D8 (88-110)	BFB (86-115)	1,2 DICHLORO-ETHANE-D4 (76-114)	NITRO-BENZENE-D5 (35-114)	2-FLUORO-BIPHENYL (43-116)	TERPHENYL-D14 (33-141)			PHENOL-D5 (10-94)	2-FLUORO-PHENOL (21-100)	2,4,6 TRIBROMO-PHENOL (10-123)	DIBUTYL-CHLORENDATE (24-154)

VALUES ARE OUTSIDE OF REQUIRED QC LIMITS

Volatiles: _____ out of _____ ; outside of QC limits
Semi-Volatiles: _____ out of _____ ; outside of QC limits
Pesticides: _____ out of _____ ; outside of QC limits

Comments: _____

_____

_____

_____

FORM II

Revision 0
Date September 1986

SOIL SURROGATE PERCENT RECOVERY SUMMARY

Case No. _____ **Laboratory Name** _____

	VOLATILE			SEMI-VOLATILE								PESTICIDE
SAMPLE NO.	TOLUENE-D8 (81-117)	BFB (74-121)	1,2 DICHLORO-ETHANE-D4 (70-121)	NITRO-BENZENE-D5 (23-120)	2-FLUORO-BIPHENYL (30-115)	TERPHENYL-D14 (18-137)			PHENOL-D5 (24-113)	2-FLUORO-PHENOL (25-121)	2,4,6 TRIBROMO-PHENOL (19-122)	DIBUTYL-CHLORENDATE (20-150)

VALUES ARE OUTSIDE OF REQUIRED QC LIMITS

Volatiles: _____ out of _____; outside of QC limits
Semi-Volatiles: _____ out of _____; outside of QC limits
Pesticides: _____ out of _____; outside of QC limits

Comments: _____

FORM II

Revision 0
Date September 1986

WATER MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Case No. _____ **Laboratory Name** _____

FRACTION	COMPOUND	CONC. SPIKE ADDED (ug/L)	SAMPLE RESULT	CONC. MS	% REC	CONC. MSD	% REC	RPD	QC LIMITS RPD	QC LIMITS RECOVERY
VOA	1,1-Dichloroethene								14	61-145
	Trichloroethene								14	71-120
SAMPLE NO.	Chlorobenzene								13	75-130
	Toluene								13	76-125
_____	Benzene								11	76-127
B/N	1,2,4-Trichlorobenzene								28	39-98
	Acenaphthene								31	46-118
	2,4 Dinitrotoluene								38	24-96
SAMPLE NO.	Di-n-Butylphthalate								40	11-117
	Pyrene								31	26-127
	N-Nitroso-Di-n-Propylamine								38	41-116
_____	1,4-Dichlorobenzene								28	36-97
ACID	Pentachlorophenol								50	9-103
	Phenol								42	12-89
	2-Chlorophenol								40	27-123
SAMPLE NO.	4-Chloro-3-Methylphenol								42	23-97
_____	4-Nitrophenol								50	10-80
PEST	Lindane								15	56-123
	Heptachlor								20	40-131
	Aldrin								22	40-120
SAMPLE NO.	Dieldrin								18	52-126
	Endrin								21	56-121
_____	4,4'-DDT								27	38-127

ADVISORY LIMITS

RPD: VOAs ____ out of ____; outside QC limits
B/N ____ out of ____; outside QC limits
ACID ____ out of ____; outside QC limits
PEST ____ out of ____; outside QC limits

RECOVERY: VOAs ____ out of ____; outside QC limits
B/N ____ out of ____; outside QC limits
ACID ____ out of ____; outside QC limits
PEST ____ out of ____; outside QC limits

Comments: _____

_____

_____

_____

_____

FORM III

Revision 0
Date September 1986

SOIL MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Case No. _____ **Laboratory Name** _____

FRACTION	COMPOUND	CONC. SPIKE ADDED (ug/Kg)	SAMPLE RESULT	CONC. MS	% REC	CONC. MSD	% REC	RPD	QC LIMITS RPD	QC LIMITS RECOVERY
VOA	1,1-Dicholorethene								22	59-172
	Trichloroethene								24	62-137
SAMPLE NO.	Chlorobenzene								21	60-133
	Toluene								21	59-139
_____	Benzene								21	66-142
B/N	1,2,4-Trichlorobenzene								23	38-107
	Acenaphthene								19	31-137
	2,4 Dinitrotoluene								47	28-89
SAMPLE NO.	Di-n-Butylphthalate								47	29-135
	Pyrene								36	35-142
	N-Nitrosodi-n-Propylamine								38	41-126
_____	1,4-Dichlorobenzene								27	28-104
ACID	Pentachlorophenol								47	17-109
	Phenol								35	26-90
	2-Chlorophenol								50	25-102
SAMPLE NO.	4-Chloro-3-Methylphenol								33	26-103
	4-Nitrophenol								50	11-114
PEST	Lindane								50	46-127
	Heptachlor								31	35-130
	Aldrin								43	34-132
SAMPLE NO.	Dieldrin								38	31-134
	Endrin								45	42-139
_____	4,4'-DDT								50	23-134

ADVISORY LIMITS

RPD: VOAs ____ out of ____; outside QC limits
B/N ____ out of ____; outside QC limits
ACID ____ out of ____; outside QC limits
PEST ____ out of ____; outside QC limits

RECOVERY: VOAs ____ out of ____; outside QC limits
B/N ____ out of ____; outside QC limits
ACID ____ out of ____; outside QC limits
PEST ____ out of ____; outside QC limits

Comments: _____

FORM III

Revision 0
Date September 1986

METHOD BLANK SUMMARY

Case No. _____ Laboratory Name _____

FILE ID	DATE OF ANALYSIS	FRACTION	MATRIX	CONC. LEVEL	INST. ID	CAS NUMBER	COMPOUND (HSL.TIC OR UNKNOWN)	CONC.	UNITS	CRDL

Comments:

FORM IV

Revision 0
Date September 1986

GC/MS TUNING AND MASS CALIBRATION

Bromofluorobenzene (BFB)

Case No. _____ Laboratory Name _____

Instrument ID _____ Date _____ Time _____

Data Release Authorized By: _____

m/e	ION ABUNDANCE CRITERIA	%RELATIVE ABUNDANCE
50	15.0 - 40.0% of the base peak	
75	30.0 - 60.0% of the base peak	
95	Base peak, 100% relative abundance	
96	5.0 - 9.0% of the base peak	
173	Less than 1.0% of the base peak	
174	Greater than 50.0% of the base peak	
175	5.0 - 9.0% of mass 174	( )[1]
176	Greater than 95.0%, but less than 101.0% of mass 174	( )[1]
177	5.0 - 9.0% of mass 176	( )[2]

THIS PERFORMANCE TUNE APPLIES TO THE FOLLOWING SAMPLES, BLANKS AND STANDARDS.

[1]Value in parenthesis is % mass 174.
[2]Value in parenthesis is % mass 176.

SAMPLE ID	LAB ID	DATE OF ANALYSIS	TIME OF ANALYSIS

FORM V

Revision 0
Date September 1986

GC/MS TUNING AND MASS CALIBRATION
Decafluorotriphenylphosphine (DFTPP)

Case No. _____ **Laboratory Name** _____

Instrument ID _____ Date _____ Time _____

Data Release Authorized By: _____

m/e	ION ABUNDANCE CRITERIA	%RELATIVE ABUNDANCE
51	30.0 - 60.0% of mass 198	
68	less than 2.0% of mass 69	( )[1]
69	mass 69 relative abundance	
70	less than 2.0% of mass 69	( )[1]
127	40.0 - 60.0% of mass 198	
197	less than 1.0% of mass 198	
198	base peak, 100% relative abundance	
199	5.0 - 9.0% of mass 198	
275	10.0 - 30.0% of mass 198	
365	greater than 1.00% of mass 198	
441	present, but less than mass 443	
442	greater than 40.0% of mass 198	
443	17.0 - 23.0% of mass 442	( )[2]

THIS PERFORMANCE TUNE APPLIES TO THE FOLLOWING SAMPLES, BLANKS AND STANDARDS.

[1]Value in parenthesis is % mass 69.
[2]Value in parenthesis is % mass 442.

SAMPLE ID	LAB ID	DATE OF ANALYSIS	TIME OF ANALYSIS

FORM V

Revision 0
Date September 1986

Initial Calibration Data
Volatile HSL Compounds

Case No: _____ Instrument I D: _____

Laboratory Name _____ Calibration Date: _____

Minimum $\overline{RF}$ for SPCC is 0.300 (0.25 for Bromoform) Maximum % RSD for CCC is 30%

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{100}	RF_{150}	RF_{200}	$\overline{RF}$	% RSD	CCC* SPCC**
Chloromethane								**
Bromomethane								
Vinyl Chloride								*
Chloroethane								
Methylene Chloride								
Acetone								
Carbon Disulfide								
1, 1-Dichloroethene								*
1, 1-Dichloroethane								**
Trans-1, 2-Dichloroethene								
Chloroform								*
1, 2-Dichloroethane								
2-Butanone								
1, 1, 1-Trichloroethane								
Carbon Tetrachloride								
Vinyl Acetate								
Bromodichloromethane								
1, 2-Dichloropropane								*
Trans-1, 3-Dichloropropene								
Trichloroethene								
Dibromochloromethane								
1, 1, 2-Trichloroethane								
Benzene								
cis-1, 3-Dichloropropene								
2-Chloroethylvinylether								
Bromoform								**
4-Methyl-2-Pentanone								
2-Hexanone								
Tetrachloroethene								
1, 1, 2, 2-Tetrachloroethane								**
Toluene								*
Chlorobenzene								**
Ethylbenzene								*
Styrene								
Total Xylenes								

RF -Response Factor (subscript is the amount of ug/L)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation

CCC -Calibration Check Compounds (*)
SPCC -System Performance Check Compounds (**)

Form VI

Initial Calibration Data
Volatile HSL Compounds

Case No: ______________ Instrument I D: __________________________

Laboratory Name _________________________ Calibration Date: __________________________

Minimum $\overline{RF}$ for SPCC is 0.300
(0.25 for Bromoform)

Maximum % RSD for CCC is 30%

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{100}	RF_{150}	RF_{200}	$\overline{RF}$	% RSD	CCC* SPCC**

RF -Response Factor (subscript is the amount of ug/L)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation

CCC -Calibration Check Compounds (*)
SPCC -System Performance Check Compounds (**)

Form VI

Initial Calibration Data
Semivolatile HSL Compounds
(Page 1)

Case No: _____ Instrument ID: _____

Laboratory Name _____ Calibration Date: _____

Minimum $\overline{RF}$ for SPCC is 0.050 Maximum % RSD for CCC is 30%

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{80}	RF_{120}	RF_{160}	$\overline{RF}$	%RSD	CCC* SPCC**
Phenol								*
bis(-2-Chloroethyl)Ether								
2-Chlorophenol								
1, 3-Dichlorobenzene								
1, 4-Dichlorobenzene								*
Benzyl Alcohol								
1, 2-Dichlorobenzene								
2-Methylphenol								
bis(2-chloroisopropyl)Ether								
4-Methylphenol								
N-Nitroso-Di-n-Propylamine								* *
Hexachloroethane								
Nitrobenzene								
Isophorone								
2-Nitrophenol								*
2, 4-Dimethylphenol								
Benzoic Acid	†							
bis(-2-Chloroethoxy)Methane								
2, 4-Dichlorophenol								*
1, 2, 4-Trichlorobenzene								
Naphthalene								
4-Chloroaniline								
Hexachlorobutadiene								*
4-Chloro-3-Methylphenol								*
2-Methylnaphthalene								
Hexachlorocyclopentadiene								* *
2, 4, 6-Trichlorophenol								*
2, 4, 5-Trichlorophenol	†							
2-Chloronaphthalene								
2-Nitroaniline	†							
Dimethyl Phthalate								
Acenaphthylene								
3-Nitroaniline	†							
Acenaphthene								*
2, 4-Dinitrophenol	†							* *
4-Nitrophenol	†							* *
Dibenzofuran								

Response Factor (subscript is the amount of nanograms)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation
CCC -Calibration Check Compounds (•)
SPCC -System Performance Check Compounds (••)
† -Not detectable at 20 ng

Form VI

Revision 0
Date September 1986

Initial Calibration Data
Semivolatile HSL Compounds
(Page 2)

Case No: _____ Instrument ID: _____

Laboratory Name _____ Calibration Date: _____

Minimum $\overline{RF}$ for SPCC is 0.050 Maximum % RSD for CCC is 30%

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{80}	RF_{120}	RF_{160}	$\overline{RF}$	% RSD	CCC* SPCC**
2, 4-Dinitrotoluene								
2, 6-Dinitrotoluene								
Diethylphthalate								
4-Chlorophenyl-phenylether								
Fluorene								
4-Nitroaniline	†							
4, 6-Dinitro-2-Methylphenol	†							
N-Nitrosodiphenylamine (1)								*
4-Bromophenyl-phenylether								
Hexachlorobenzene								
Pentachlorophenol	†							*
Phenanthrene								
Anthracene								
Di-N-Butylphthalate								
Fluoranthene								*
Pyrene								
Butylbenzylphthalate								
3, 3'-Dichlorobenzidine								
Benzo(a)Anthracene								
bis(2-Ethylhexyl)Phthalate								
Chrysene								
Di-n-Octyl Phthalate								*
Benzo(b)Fluoranthene								
Benzo(k)Fluoranthene								
Benzo(a)Pyrene								*
Indeno(1, 2, 3-cd)Pyrene								
Dibenz(a, h)Anthracene								
Benzo(g, h, i)Perylene								

Response Factor (subscript is the amount of nanograms)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation
CCC -Calibration Check Compounds (*)
SPCC -System Performance Check Compounds (**)
† - Not detectable at 20 ng
(1) -Cannot be separated from diphenylamine

Form VI

Revision 0
Date September 1986

Initial Calibration Data
Semivolatile HSL Compounds
(Page 1)

Case No: ____________ Instrument ID: ____________________________

Laboratory Name ________________________ Calibration Date: ____________________________

Minimum $\overline{RF}$ for SPCC is **0.050** Maximum % RSD for CCC is **30%**

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{80}	RF_{120}	RF_{160}	$\overline{RF}$	% RSD	CCC• SPCC••

Response Factor (subscript is the amount of nanograms)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation
CCC -Calibration Check Compounds (•)
SPCC -System Performance Check Compounds (••)
† -Not detectable at 20 ng

Form VI

Continuing Calibration Check
Volatile HSL Compounds

Case No: _____ Calibration Date: _____

Laboratory Name _____ Time: _____

Contract No: _____ Laboratory ID: _____

Instrument ID: _____ Initial Calibration Date: _____

Minimum RF for SPCC is 0.300 (0.25 for Bromoform) Maximum %D for CCC is 25%

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC
Chloromethane					**
Bromomethane					
Vinyl Chloride				*	
Chloroethane					
Methylene Chloride					
Acetone					
Carbon Disulfide					
1, 1-Dichloroethene				*	
1, 1-Dichloroethane					**
Trans-1, 2-Dichloroethene					
Chloroform				*	
1, 2-Dichloroethane					
2-Butanone					
1, 1, 1-Trichloroethane					
Carbon Tetrachloride					
Vinyl Acetate					
Bromodichloromethane					
1, 2-Dichloropropane				*	
Trans-1, 3-Dichloropropene					
Trichloroethene					
Dibromochloromethane					
1, 1, 2-Trichloroethane					
Benzene					
cis-1, 3-Dichloropropene					
2-Chloroethylvinylether					
Bromoform					**
4-Methyl-2-Pentanone					
2-Hexanone					
Tetrachloroethene					
1, 1, 2, 2-Tetrachloroethane					**
Toluene				*	
Chlorobenzene					**
Ethylbenzene				*	
Styrene					
Total Xylenes					

RF_{50} -Response Factor from daily standard file at 50 ug/l
RF -Average Response Factor from initial calibration Form VI

%D -Percent Difference
CCC -Calibration Check Compounds (*)
SPCC -System Performance Check Compounds (**)

Form VII

Revision 0
Date September 1986

Continuing Calibration Check
Volatile HSL Compounds

Case No: ____________ Calibration Date: ____________

Laboratory Name ____________ Time: ____________

Contract No: ____________ Laboratory ID: ____________

Instrument ID: ____________ Initial Calibration Date: ____________

Minimum RF for SPCC is 0.300 (0.25 for Bromoform) Maximum %D for CCC is **25%**

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC

RF_{50} - Response Factor from daily standard file at 50 ug/l
$\overline{RF}$ - Average Response Factor from initial calibration Form VI

%D - Percent Difference
CCC - Calibration Check Compounds (•)
SPCC - System Performance Check Compounds (••)

Form VII

Continuing Calibration Check
Semivolatile HSL Compounds
(Page 1)

Case No: _____ Calibration Date: _____

Laboratory Name_____ Time: _____

Laboratory ID: _____

Instrument ID: _____ Initial Calibration Date: _____

Minimum RF for SPCC is 0.050 Maximum %D for CCC is 25%

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC
Phenol				*	
bis(-2-Chloroethyl)Ether					
2-Chlorophenol					
1, 3-Dichlorobenzene					
1, 4-Dichlorobenzene				*	
Benzyl Alcohol					
1, 2-Dichlorobenzene					
2-Methylphenol					
bis(2-chloroisopropyl)Ether					
4-Methylphenol					
N-Nitroso-Di-n-Propylamine					**
Hexachloroethane					
Nitrobenzene					
Isophorone					
2-Nitrophenol				*	
2, 4-Dimethylphenol					
Benzoic Acid †					
bis(-2-Chloroethoxy)Methane					
2, 4-Dichlorophenol				*	
1, 2, 4-Trichlorobenzene					
Naphthalene					
4-Chloroaniline					
Hexachlorobutadiene				*	
4-Chloro-3-Methylphenol				*	
2-Methylnaphthalene					
Hexachlorocyclopentadiene					**
2, 4, 6-Trichlorophenol				*	
2, 4, 5-Trichlorophenol †					
2-Chloronaphthalene					
2-Nitroaniline †					
Dimethyl Phthalate					
Acenaphthylene					
3-Nitroaniline †					
Acenaphthene				*	
2, 4-Dinitrophenol †					**
4-Nitrophenol †					**
Dibenzofuran					

RF_{50} -Response Factor from daily standard file at concentration indicated (50 total nanograms)

$\overline{RF}$ -Average Response Factor from initial calibration Form VI

†-Due to low response, analyze at 80 total nanograms

%D -Percent Difference

CCC -Calibration Check Compounds (•)

SPCC -System Performance Check Compounds (••)

Continuing Calibration Check
Semivolatile HSL Compounds
(Page 2)

Case No: _____ Calibration Date: _____

Laboratory Name _____ Time: _____

Laboratory ID: _____

Instrument ID: _____ Initial Calibration Date: _____

Minimum RF for SPCC is 0.050 Maximum %D for CCC is 25%

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC
2, 4-Dinitrotoluene					
2, 6-Dinitrotoluene					
Diethylphthalate					
4-Chlorophenyl-phenylether					
Fluorene					
4-Nitroaniline †					
4, 6-Dinitro-2-Methylphenol †					
N-Nitrosodiphenylamine (1)				*	
4-Bromophenyl-phenylether					
Hexachlorobenzene					
Pentachlorophenol †				*	
Phenanthrene					
Anthracene					
Di-N-Butylphthalate					
Fluoranthene				*	
Pyrene					
Butylbenzylphthalate					
3, 3'-Dichlorobenzidine					
Benzo(a)Anthracene					
bis(2-Ethylhexyl)Phthalate					
Chrysene					
Di-n-Octyl Phthalate				*	
Benzo(b)Fluoranthene					
Benzo(k)Fluoranthene					
Benzo(a)Pyrene				*	
Indeno(1, 2, 3-cd)Pyrene					
Dibenz(a, h)Anthracene					
Benzo(g, h, i)Perylene					

RF_{50} -Response Factor from daily standard file at concentration indicated (50 total nanograms)

$\overline{RF}$ -Average Response Factor from initial calibration Form VI

%D Percent Difference

† -Due to low response, analyze at 80 total nanograms

CCC -Calibration Check Compounds (•)

SPCC -System Performance Check Compounds (••)

(1) -Cannot be separated from diphenylamine

Form VII

Revision 0
Date September 1986

Continuing Calibration Check
Semivolatile HSL Compounds
(Page 1)

Case No: ____________ Calibration Date: ____________

Laboratory Name ____________ Time: ____________

Laboratory ID: ____________

Instrument ID: ____________ Initial Calibration Date: ____________

Minimum RF for SPCC is 0.050 Maximum %D for CCC is 25%

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC

RF_{50} -Response Factor from daily standard file at concentration indicated (50 total nanograms)

$\overline{RF}$ -Average Response Factor from initial calibration Form VI

† -Due to low response, analyze at 80 total nanograms

%D -Percent Difference

CCC -Calibration Check Compounds (•)

SPCC System Performance Check Compounds (••)

Form VII

Pesticide Evaluation Standards Summary
(Page 1)

Case No: _____ **Laboratory Name**: _____

GC Column: _____

Date of Analysis: _____ Instrument ID: _____

Evaluation Check for Linearity

Laboratory ID				
Pesticide	Calibration Factor Eval. Mix A	Calibration Factor Eval. Mix B	Calibration Factor Eval. Mix C	% RSD (≤10%)
Aldrin				
Endrin				
4,4'- DDT[1]				
Dibutyl Chlorendate				

Evaluation Check for 4,4'- DDT/Endrin Breakdown
(percent breakdown expressed as total degradation)

	Laboratory I.D.	Time of Analysis	Endrin	4,4'- DDT	Combined[2]
Eval Mix B 72 Hour					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					

(1) See Exhibit E, Section 7.5.4
(2) See Exhibit E, Section 7.3.1.2.2.1

Pesticide Evaluation Standards Summary
(Page 2)

Evaluation of Retention Time Shift for Dibutyl Chlorendate

Report all standards, blanks and samples

Sample No	Lab I.D.	Time of Analysis	Percent Diff.	SMO Sample No.	Lab I.D.	Time of Analysis	Percent Diff.

Form VIII (Continued)

RCRA
4/86

PESTICIDE/PCB STANDARDS SUMMARY

Case No. _____ Laboratory Name _____

GC Column _____ GC Instrument ID _____

	DATE OF ANALYSIS _____ TIME OF ANALYSIS _____ LABORATORY ID _____				DATE OF ANALYSIS _____ TIME OF ANALYSIS _____ LABORATORY ID _____			
COMPOUND	RT	RETENTION TIME WINDOW	CALIBRATION FACTOR	CONF. OR QUANT.	RT	CALIBRATION FACTOR	CONF. OR QUANT.	PERCENT DIFF.**
alpha-BHC								
beta-BHC								
delta-BHC								
gamma-BHC								
Heptachlor								
Aldrin								
Heptachlor Epoxide								
Endosulfan I								
Dieldrin								
4,4'-DDE								
Endrin								
Endosulfan II								
4,4'-DDD								
Endrin Aldehyde								
Endosulfan Sulfate								
4,4'-DDT								
Methoxychlor								
Endrin Ketone								
Tech. Chlordane								
alpha-Chlordane								
gamma-Chlordane								
Toxaphene								
Aroclor - 1016								
Aroclor - 1221								
Aroclor - 1232								
Aroclor - 1242								
Aroclor - 1248								
Aroclor - 1254								
Aroclor - 1260								

** CONF. = CONFIRMATION (<20% DIFFERENCE)
QUANT. = QUANTITATION (<15% DIFFERENCE)

FORM IX

Revision 0
Date September 1986

Pesticide/PCB Identification

Case No. ______________________ Laboratory Name ______________________

SAMPLE ID	PRIMARY COLUMN	PESTICIDE/ PCB	RT OF TENTATIVE ID	RT WINDOW OF APPROPRIATE STANDARD	CONFIRMATION COLUMN	RT ON CONFIRMATORY COLUMN	RT WINDOW OF APPROPRIATE STANDARD	GC/MS CONFIRMED (Y or N)

FORM X

CHAPTER TWO

CHOOSING THE CORRECT PROCEDURE

2.1 PURPOSE

This chapter aids the analyst in choosing the appropriate methods for samples, based upon sample matrix and the analytes to be determined.

2.2 REQUIRED INFORMATION

In order to choose the correct combination of procedures to form the appropriate analytical method, some basic information is required.

2.2.1 Physical State(s) of Sample

The phase characteristics of the sample must be known. There are several general categories of phases in which the sample may be categorized:

- Aqueous
- Oil and Organic Liquid
- Sludges
- Solids
- Multiphase Samples
- EP and TCLP Extracts
- Ground Water.

2.2.2 Analytes

Analytes are divided into classes based on the determinative methods which are used to identify and quantify them. The organic compounds are divided into different groups as indicated by Tables 2-1 through 2-14. Some of the analytes appear on more than one table, as they may be determined using any of several methods.

2.2.3 Detection Limits Required

Regulations may require a specific sensitivity or detection limit for an analysis, as in the determination of analytes for the Extraction Procedure (EP) or for delisting petitions. Drinking water detection limits, for those specific organic and metallic analytes covered by the National Interim Primary Drinking Water Standards, are desired in the analysis of ground water. Table 2-15 lists those analytes which are determined under the ground water monitoring guidance. It also includes detection limits for ground water monitoring and for the EP and TCLP procedures.

2.2.4 Analytical Objective

Knowledge of the analytical objective will be useful in the choice of sub-sampling procedures and in the selection of a determinative method. This is especially true when the sample has more than one phase. Knowledge of the analytical objective may not be possible or desirable at all management levels, but that information should be transmitted to the analytical laboratory management to ensure that the correct techniques are being applied to the analytical effort.

2.2.5 Detection and Monitoring

The strategy for detection of compounds in environmental or process samples may be contrasted with the strategy for monitoring samples. Detection samples define initial conditions. When there is little information available about the composition of the sample source, e.g., a well or process stream, mass spectral identification of organic analytes leads to fewer false positive results. Thus, the most practical form of detection for organic analytes, given the analytical requirements, is mass spectral identification. The choice of technique for metals is governed by the detection limit requirements and potential interferents.

Monitoring samples, on the other hand, are analyzed to confirm existing and on-going conditions, tracking the presence or absence of constituents in an environmental or process matrix. A less compound(s)-specific detection mode may be used because the matrix and the analytical conditions are well defined and stable.

2.2.6 Sample Containers, Preservations, and Holding Times

Appropriate sample containers, sample preservation techniques, and sample holding times are listed in Table 2-16, at the end of this chapter.

2.3 IMPLEMENTING THE GUIDANCE

The choice of the appropriate sequence of methods depends on the information required and on the analyst's experience. Figure 2-1 summarizes the organic analysis options available. Appropriate selection is confirmed by the quality control results. The use of the recommended procedures, whether they are approved or mandatory, does not release the analyst from demonstrating the correct execution of the method.

2.3.1 Determinative Procedures

The determinative methods for organic analytes have been divided into three categories, shown in Figure 2-2: gas chromatography (GC); gas chromatography/mass spectrometry (GC/MS); and high pressure liquid chromatography (HPLC). This division is intended to help an analyst choose which determinative method will apply. Under each analyte column, SW-846 method numbers have been indicated, if appropriate, for the determination of the analyte. A blank has been left if no chromatographic determinative method is available.

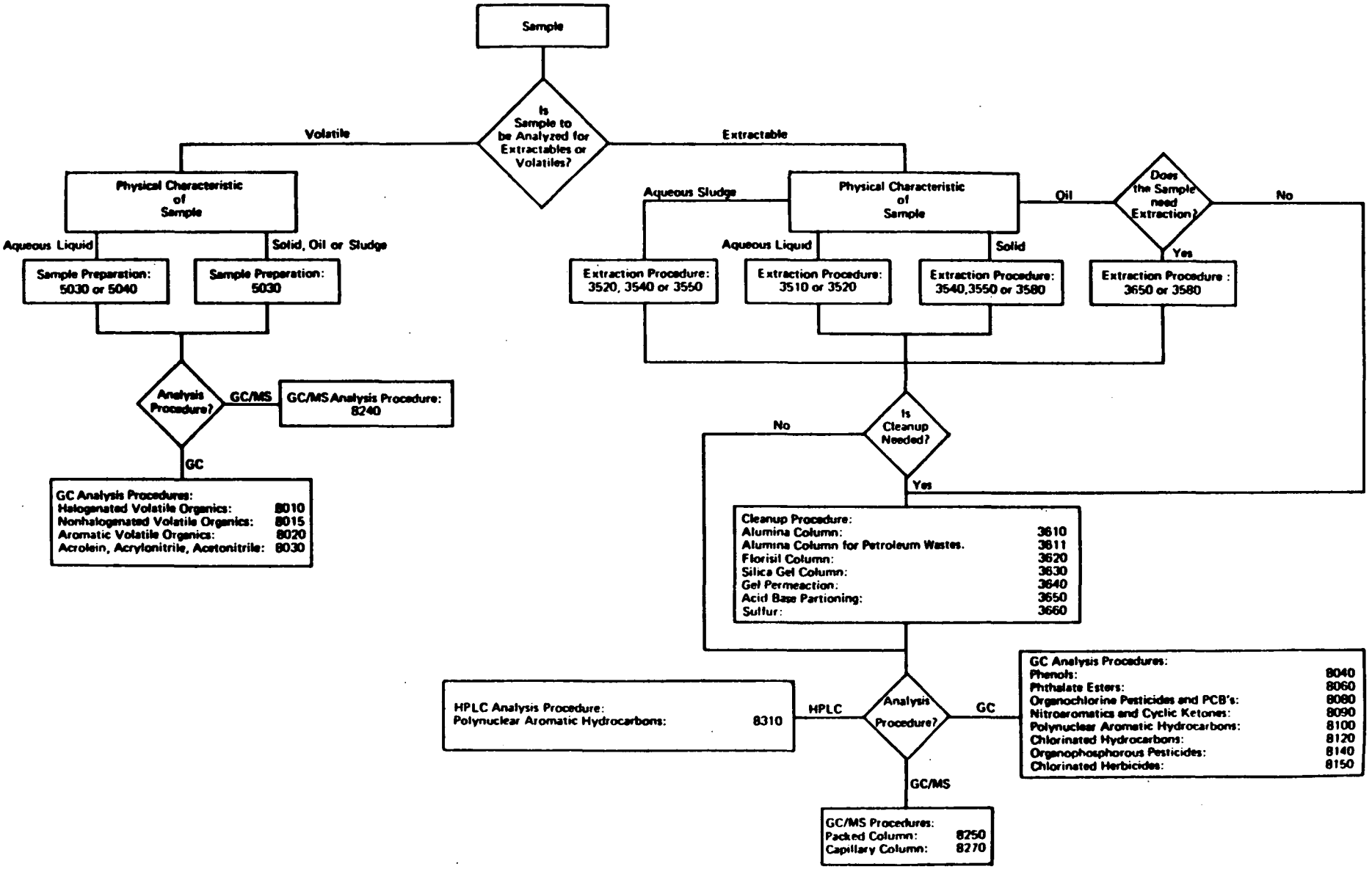


Figure 2-1. Organic Analysis Options

	Semivolatile Organic Compounds									
	Phenols	Acids	Phthalate Esters	Nitro-aromatics & Cyclic Ketones	Polyaromatic hydrocarbons	Chlorinated hydrocarbons	Base/Neutral	Organo-phosphorous Pesticides	Organo-chlorine Pesticides & PCBs	Chlorinated Herbicides
GC/MS Determination Methods	8270 8250	8270 8250	8270 8250	8270 8250	8270 8250	8270 8250	8270 8250	8270*	8270*	8270*
Specific Detection Methods	8040		8060	8090	8100	8120		8140	8080	8150
HPLC					8310					

*This method is an alternative confirmation method. It is not the method of choice.

Figure 2-2. Determination of Organic Analytes.

	Volatile Organic Compounds				
	Halogenated Volatiles	Non-halogenated Volatiles	Aromatic Volatiles	Acrolein Acrylonitrile Acetonitrile	Volatile Organics
GC/MS Determination Methods	8240	8240	8240	8240	8240
Specific Detection Methods	8010	8015	8020	8030	
HPLC					

Figure 2-2. Determination of Organic Analytes. (Continued)

Generally, the MS procedures are more specific but less sensitive than the appropriate gas chromatographic/specific detection method.

Method 8140, for organophosphorous pesticides, and Method 8150, for chlorinated herbicides, are preferred to GC/MS because of the combination of selectivity and sensitivity of the flame photometric and electron capture detectors.

Methods 8250 and 8270 are both semivolatile GC/MS methods. Method 8250 uses a packed column whereas Method 8270 employs a capillary column. Better chromatographic separation of the semivolatile compounds may be obtained by using Method 8270 rather than 8250. Performance criteria will be based on Method 8270.

For volatile organic compounds, Method 8240 is the determinative procedure. Method 5030 has been combined with Method 8240, with which it was used exclusively. A GC with a selective detector is also useful for the determination of volatile organic compounds in a monitoring scenario, described in Section 2.2.5.

Method 8000 gives a general description of the method of gas chromatography. This method should be consulted prior to application of any of the gas chromatographic methods.

2.3.2 Cleanup Procedures

Each category in Figure 2-3, Cleanup of Organic Analyte Extracts, corresponds to one of the possible determinative methods available in the manual. Cleanups employed are determined by the analytes of interest within the extract. However, the necessity of performing cleanup may also depend upon the matrix from which the extract was developed. Cleanup of a sample may be done exactly as instructed in the cleanup method for some of the analytes. There are some instances when cleanup using one of the methods may only proceed after the procedure is modified to optimize recovery and separation. Several cleanup techniques may be possible for each analyte category. The information provided is not meant to imply that any or all of these methods must be used for the analysis to be acceptable. Extracts with components which interfere with spectral or chromatographic determinations are expected to be subjected to cleanup procedures.

The analyst's discretion must determine the necessity for cleanup procedures, as there are no clear cut criteria for indicating their use. Method 3600 and associated procedures should be consulted for further details on employing cleanup procedures.

2.3.3 Extraction and Sample Preparation Procedures

Methods for preparing organic analytes are shown in Figure 2-4. Method 3500 and associated procedures should be consulted for further details on preparing the sample for analysis.

Phenols	Acids	Phthalate Esters	Nitro-aromatics & Cyclic Ketones	Polyaromatic hydrocarbons	Chlorinated hydrocarbons	Base/Neutral	Organo-phosphorous Pesticides	Organo-chlorine Pesticides & PCBs	Chlorinated Herbicides
						3620			
3630		3610		3611		3640		3620	
3640	3640	3620	3620	3630	3620	3650	3620	3640	
3650	3650	3640	3640	3640	3640	3660	3640	3660	8150

Figure 2-3. Cleanup of Organic Analyte Extracts.

	Phenols	Acids	Phthalate Esters	Nitro-aromatics & Cyclic Ketones	Polyaromatic hydrocarbons	Chlorinated hydrocarbons	Base/Neutral
Aqueous	3510 3520	3510 3520	3510 3520	3510 3520	3510 3520	3510 3520	3510 3520
pH[3]	≤2	≤2	Neutral	5-9	Neutral	Neutral	>11
Solids	3540 3550 3580[2]	3540 3550 3580[2]	3540 3550 3580[2]	3540 3550 3580[2]	3540 3550 3580[2]	3540 3550 3580[2]	3540 3550 3580[2]
Sludges: Aqueous	See Aqueous Above						
Sludges: Emulsions[1]	3520	3520	3520	3520	3520	3520	3520
Sludges: pH[3]	≤2	≤2	Neutral	5-9	Neutral	Neutral	>11
Sludges: Solids	See Solids Above						
Oils	3650 3580[2]	3650 3580[2]	3580[2]	3580[2]	3560 3580[2]	3580[2]	3650 3580[2]

[1]If attempts to break up emulsions are unsuccessful, this method may be used.
[2]Waste dilution, Method 3580, is only appropriate if the sample is soluble in the specified solvent.
[3]pH at which extraction should be performed.

Figure 2-4. Preparation Methods for Organic Analytes.

	Organo-phosphorous Pesticides	Organo-chlorine Pesticides & PCBs	Chlorinated Herbicides	Halogenated Volatiles	Non-halogenated Volatiles	Aromatic Volatiles	Acrolein Acrylonitrile Acetonitrile	Volatile Organics
Aqueous	3510 3520	3510 3520	8150	5030	5030	5030	5030	5030
pH[3]	6-8	5-9	≤2					
Solids	3540 3550 3580[2]	3540 3550 3580[2]	8150 3580[2]	5030	5030	5030	5030	5030
Aqueous	See Aqueous Above							
Sludges Emulsions[1]	3520	3520	8150	5030	5030	5030	5030	5030
pH[3]	6-8	5-9	≤2					
Solids	See Solids Above							
Oils	3580[2]	3580[2]	3580[2]	5030	5030	5030	5030	5030

Figure 2-4. Preparation Methods for Organic Analytes. (Continued)

2.3.3.1 Aqueous Samples

The choice of a preparative method depends on the sample. Methods 3510 and 3520 may be used for extraction of the semivolatile organic compounds. Method 3510, a separatory funnel extraction, is appropriate for samples which will not form a persistent emulsion interphase between the sample and the extraction solvent. The formation of an emulsion that can not be broken up by mechanical techniques will prevent proper extraction of the sample. Method 3520, a liquid-liquid continuous extraction, may be used for any aqueous sample; this method will minimize emulsion formation.

2.3.3.1.1 Basic or Neutral Extraction of Semivolatiles

The solvent extract obtained by performing either Method 3510 or 3520 at a neutral or basic pH will contain the compounds of interest. Refer to Table 1 in the extraction methods (3510 and/or 3520) for guidance on the extraction pH requirements for analysis.

2.3.3.1.2 Acidic Extraction of Phenols and Acids

The extract obtained by performing either Method 3510 or 3520 at pH 2 will contain the phenols and acid extractables.

2.3.3.2 Solid Samples

Soxhlet (Method 3540) and sonication (Method 3550) extraction are used with solid samples. Consolidated samples should be ground finely enough to pass through a 9.5 mm sieve. In limited applications, waste dilution (Method 3580) may be used if the entire sample is soluble in the specified solvent.

Method 3540 and 3550 are neutral-pH extraction techniques and therefore, depending on the analysis requirements, acid-base partition cleanup (Method 3650) may be necessary. Method 3650 will only be needed if chromatographic interferences are severe enough to prevent detection of the analytes of interest. This separation will be most important if a GC method is chosen for analysis of the sample. If GC/MS is used, the ion selectivity of the technique may compensate for chromatographic interferences.

2.3.3.3 Oils and Organic Liquids

Method 3580, waste dilution, may be used and the resultant sample analyzed directly by GC or GC/MS. To avoid overloading the analytical detection system, care must be exercised to ensure that proper dilutions are made. Method 3580 gives guidance on performing waste dilutions.

To remove interferences, Method 3611 may be performed on an oil sample directly, without prior sample preparation.

Method 3650 is the only other preparative procedure for oils and other organic liquids. This procedure is a back extraction into an aqueous phase. It is generally introduced as a cleanup procedure for extracts rather than as a preparative procedure. Oils generally have a high concentration of semivolatile compounds and, therefore, preparation by Method 3650 should be done on a relatively small aliquot of the sample. Generally, extraction of 1 mL of oil will be sufficient to obtain a saturated aqueous phase and avoid emulsions.

2.3.3.4 Sludge Samples

There is no set ratio of liquid to solid which enables the analyst to determine which of the three extraction methods cited is the most appropriate. If the sludge is an organic sludge (solid material and organic liquid, as opposed to an aqueous sludge), the sample should be handled as a multiphase sample.

Determining the appropriate methods for analysis of sludges is complicated because of the lack of precise definition of sludges with respect to the relative percent of liquid and solid components. They may be classified into three categories but with appreciable overlap.

2.3.3.4.1 Liquids

Use of Method 3510 or Method 3520 may be applicable to sludges that behave like and have the consistency of aqueous liquids. Ultrasonication (Method 3550) and soxhlet (Method 3540) procedures will, most likely, be ineffective because of the overwhelming presence of the liquid aqueous phase.

2.3.3.4.2 Solids

Soxhlet (Method 3540) and sonication (Method 3550) will be more effective when applied to sludge samples that resemble solids. Samples may be dried or centrifuged to form solid materials for subsequent determination of semivolatile compounds.

Using Method 3650, Acid-Base Partition Cleanup, on the extract may be necessary, depending on whether chromatographic interferences prevent determination of the analytes of interest.

2.3.3.4.3 Emulsions

Attempts should be made to break up and separate the phases of an emulsion. Several techniques are effective in breaking emulsions or separating the phases of emulsions.

1. Freezing/thawing: Certain emulsions will separate if exposed to temperatures below 0°C.

2. Salting out: Addition of a salt to make the aqueous phase of an emulsion too polar to support a less polar phase promotes separation.

3. Centrifugation: Centrifugal force may separate emulsion components by density.

4. Addition of water or ethanol: Emulsion polymers may be destabilized when a preponderance of the aqueous phase is added.

If techniques for breaking emulsions fail, use Method 3520. If the emulsion can be broken, the different phases (aqueous, solid, or organic liquid) may then be analyzed separately.

2.3.3.5 Multiphase Samples

Choice of the procedure for sub-sampling multiphase samples is very dependent on the objective of the analysis. With a sample in which some of the phases tend to separate rapidly, the percent weight or volume of each phase should be calculated and each phase should be individually analyzed for the required analytes. The appropriate sample matrix figure should be consulted.

An alternate approach is to obtain a homogeneous sample and attempt a single analysis on the combination of phases. This approach will give no information on the abundance of the analytes in the individual phases other than what can be implied by solubility.

A third alternative is to select phases of interest and to analyze only those selected phases. This tactic must be consistent with the sampling/analysis objectives or it will yield insufficient information for the time and resources expended. The phases selected should be compared with Figures 2-1 through 2-4 for further guidance.

2.4 CHARACTERISTICS

Figure 2-5 outlines the testing sequence for determining if a waste is hazardous by characteristics.

2.4.1 EP and TCLP extracts

The leachate obtained from using either the EP (Figure 2-6A) or the TCLP (Figure 2-6B) is an aqueous sample and, therefore, requires further solvent extraction prior to the analysis of semivolatile compounds. Figure 3 gives further information on aqueous sample extraction.

The TCLP leachate is solvent extracted with methylene chloride at a pH >11 by either Method 3510 or 3520. Method 3510 should be used unless the formation of emulsions between the sample and the solvent prevent proper extraction. If this problem is encountered, Method 3520 should be employed.

The solvent extract obtained by performing either Method 3510 or 3520 at a basic or neutral pH will contain the base/neutral compounds of interest. Refer to the specific determinative method for guidance on the extraction pH requirements for analysis. When all semivolatile analytes are being determined, the pH is then made acidic and the extraction is repeated (Method 3510 or 3520).

Due to the high concentration of acetate in the TCLP extract, it is recommended that purge-and-trap/GC/MS, Method 8240, be used to introduce the volatile sample into the gas chromatograph.

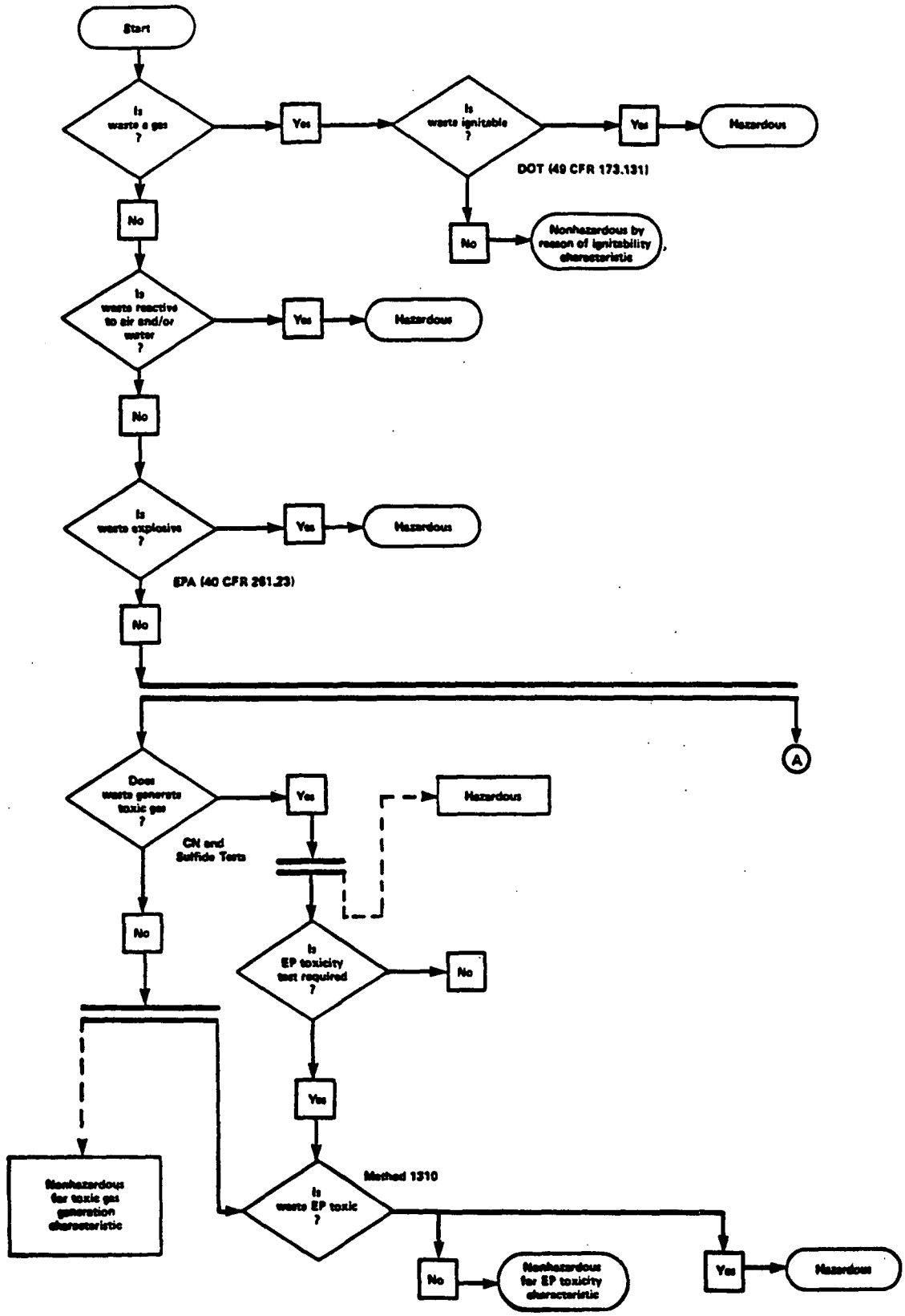


Figure 2-5. Schematic of Sequence of Testing to Determine if a Waste is Hazardous by Characteristics.

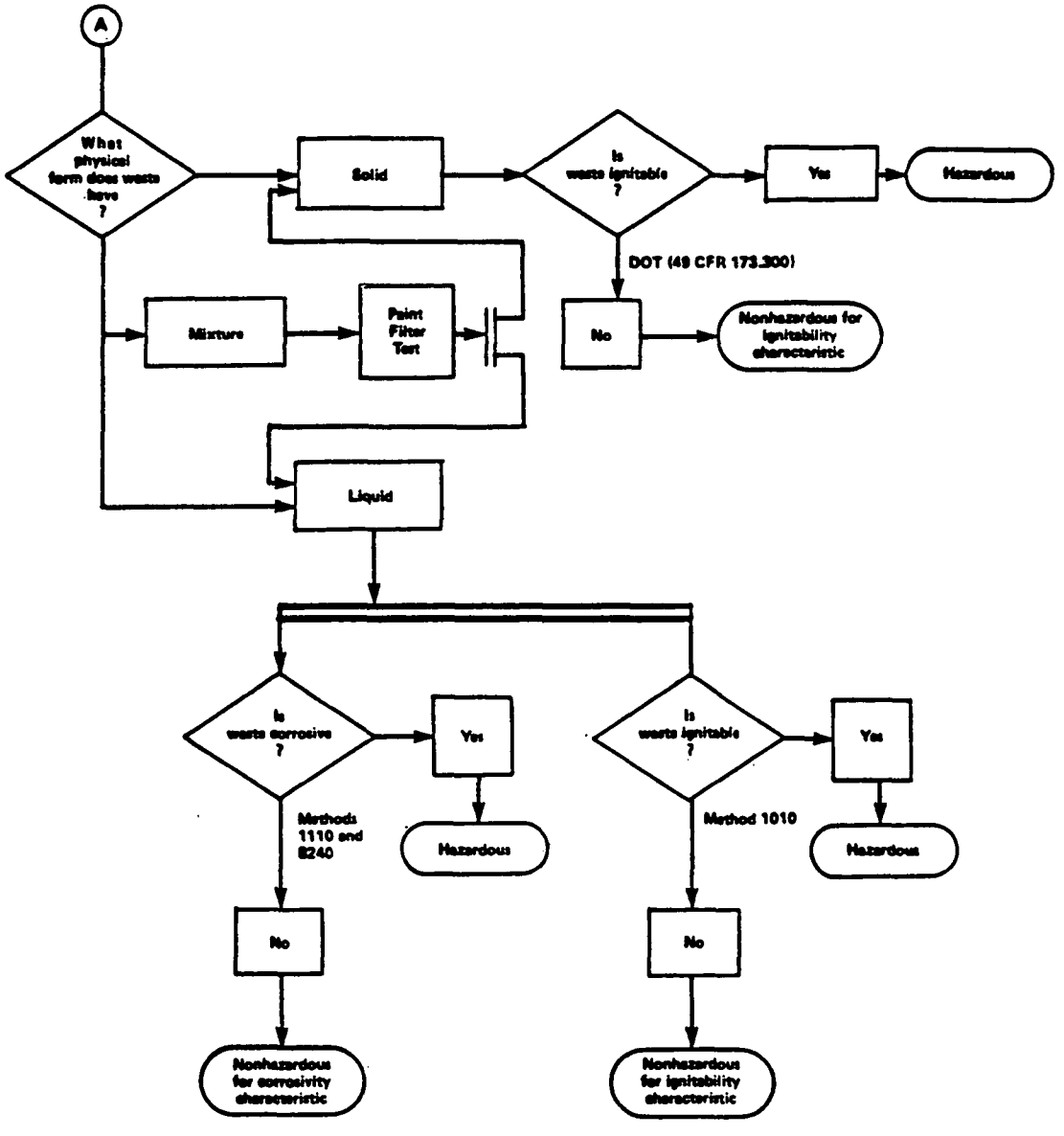


Figure 2-5. (Continued).

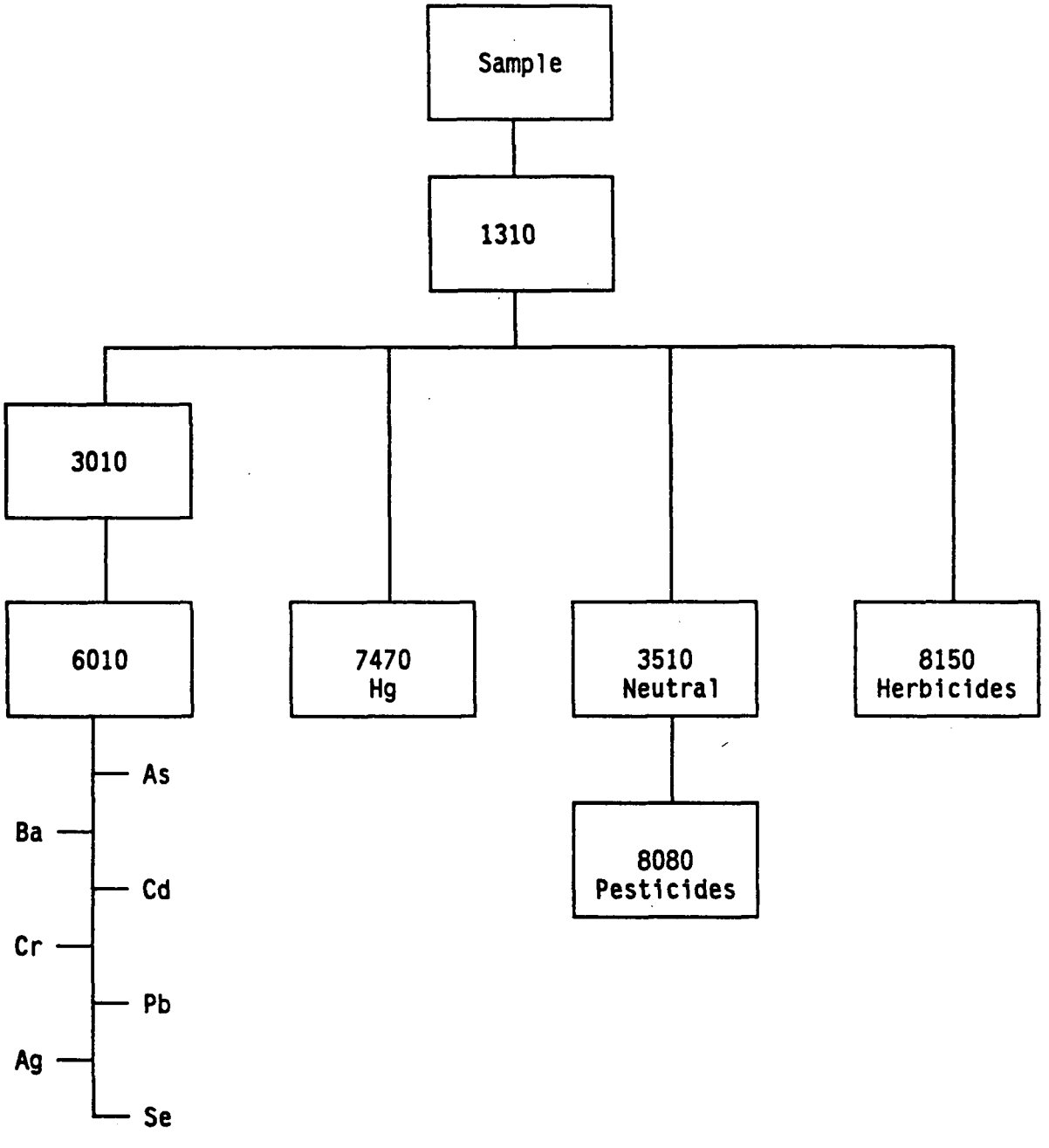


Figure 2-6A. EP.

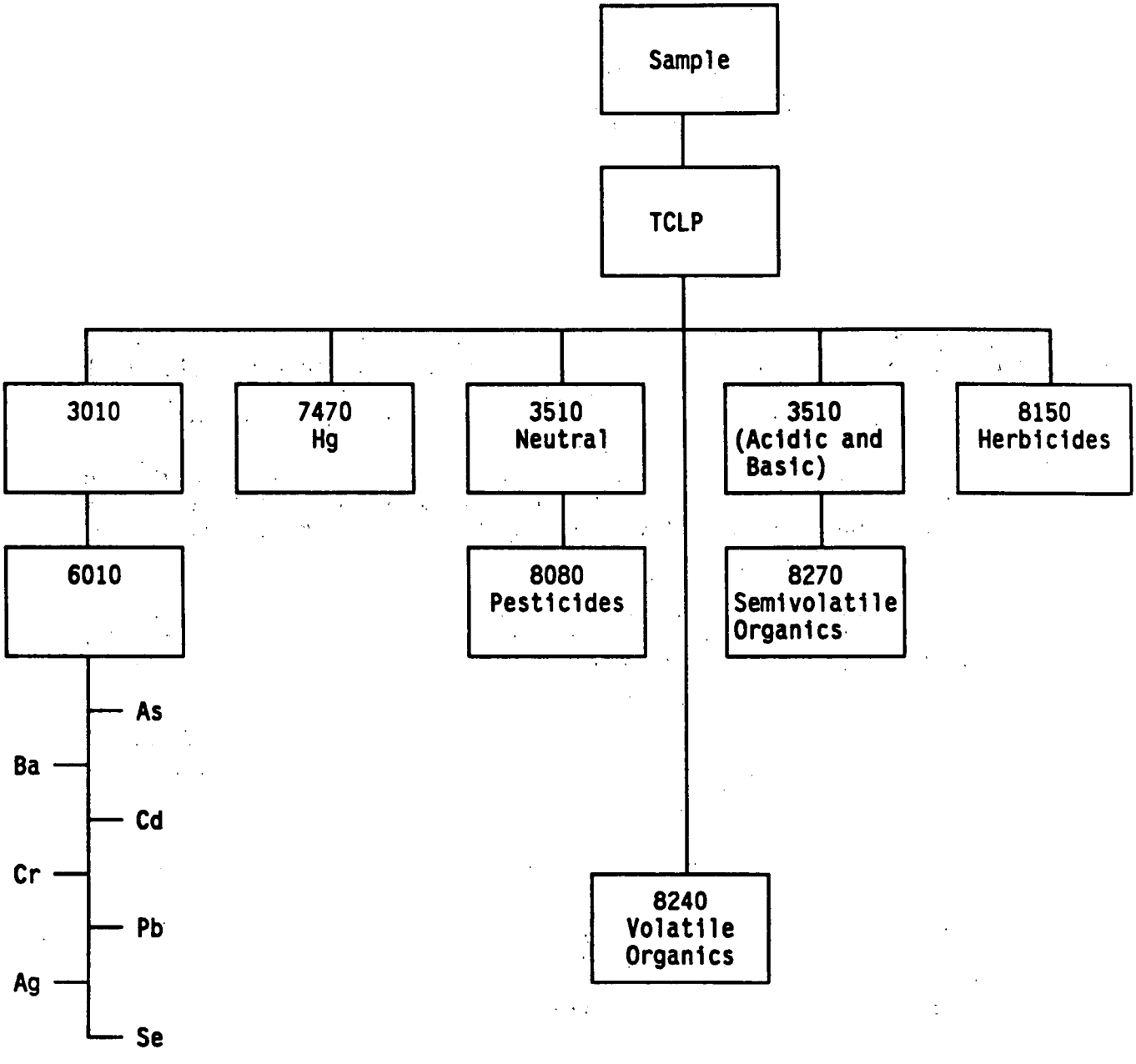


Figure 2-6B. TCLP.

2.5 GROUND WATER

Appropriate analysis schemes for the determination of analytes in ground water are presented in Figures 2-7A, 2-7B, and 2-7C. Quantitation limits for the metallic analytes should correspond to the drinking water limits which are available. These are presented, along with the quantitative limits for herbicides and anions, in Table 2-15. Nominal detection limits achievable for volatile organic compounds and the semi-volatile compounds are given, based on the indicated methods for ground water monitoring.

2.5.1 Special Techniques for Metal Analytes

All atomic absorption analyses should be performed using Zeeman or Smith-Hieftje background correction. These types of background correction will allow analysis for low level selenium in the presence of high levels of iron. They are superior to the deuterium arc background correction technique.

All graphite furnace atomic absorption (GFAA) analyses should be performed using the Lvov platform technique. This technique reduces matrix interferences and should improve the results for those elements analyzed by furnace atomic absorption.

Cadmium and antimony should be determined by GFAA. These two elements are analyzed by GFAA to achieve lower detection limits. Typical GFAA detection limits for antimony and cadmium are 3 ug/L and 0.1 ug/L, compared to 60 ug/L and 3 ug/L by ICP.

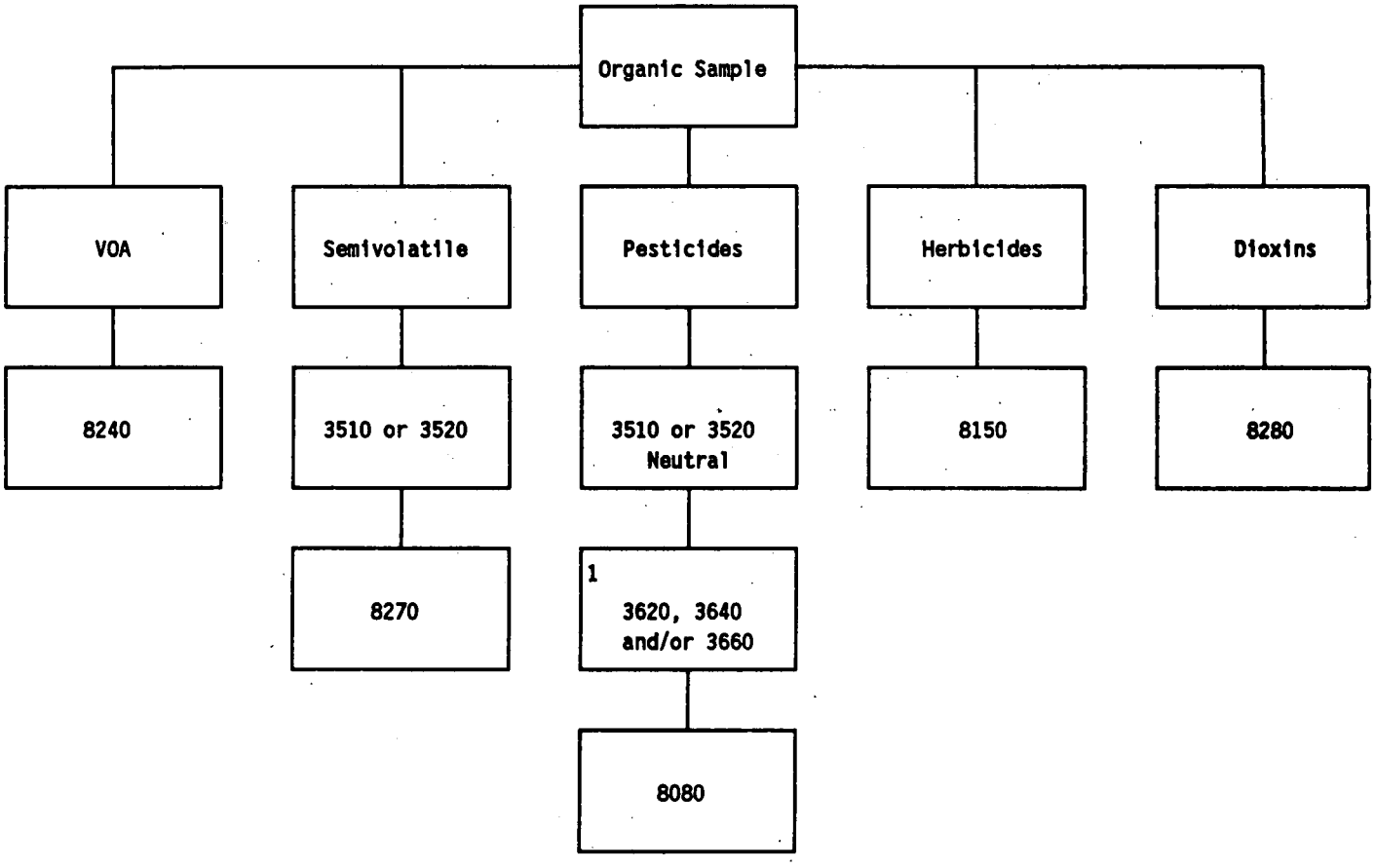
All furnace atomic absorption analysis should be carried out using the exact matrix modifiers listed below. (See also the appropriate methods.)

Element(s)	Modifier
As and Se	Nickel Nitrate
Pb	Phosphoric Acid
Cd	Ammonium Phosphate
Sb	Ammonium Nitrate
Tl	Platinum/Palladium

The ICP calibration standards must match the acid composition and strength of the acids contained in the samples. Acid strengths in the ICP calibration standards should be stated in the raw data.

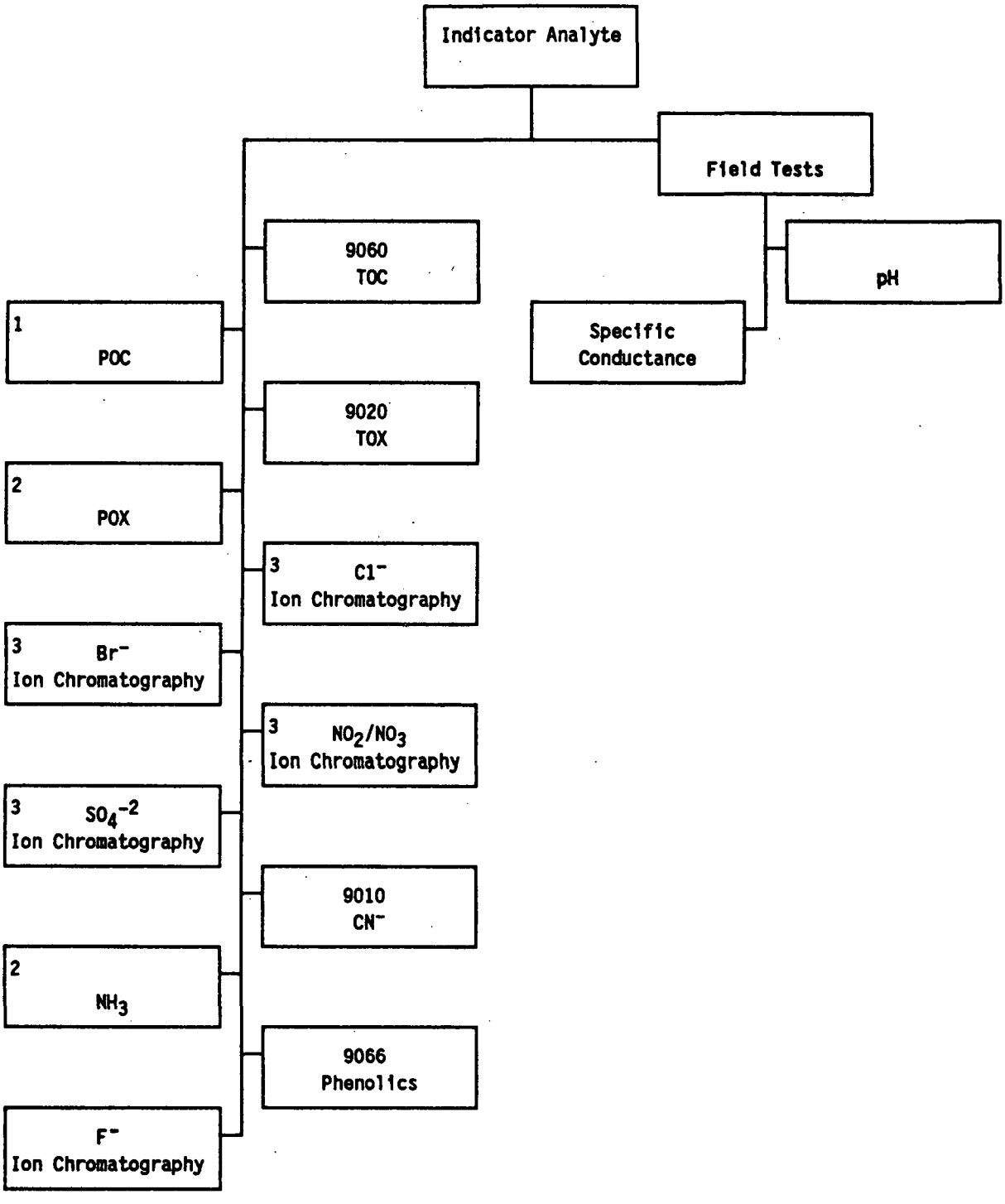
2.5.2 Special Techniques for Indicated Analytes and Anions

If an Auto-Analyzer is used to read the cyanide distillates, the spectrophotometer must be used with a 50-mm path length cell. If a sample is found to contain cyanide, the sample must be redistilled a second time and analyzed to confirm the presence of the cyanide. The second distillation must fall within the 14-day holding time.



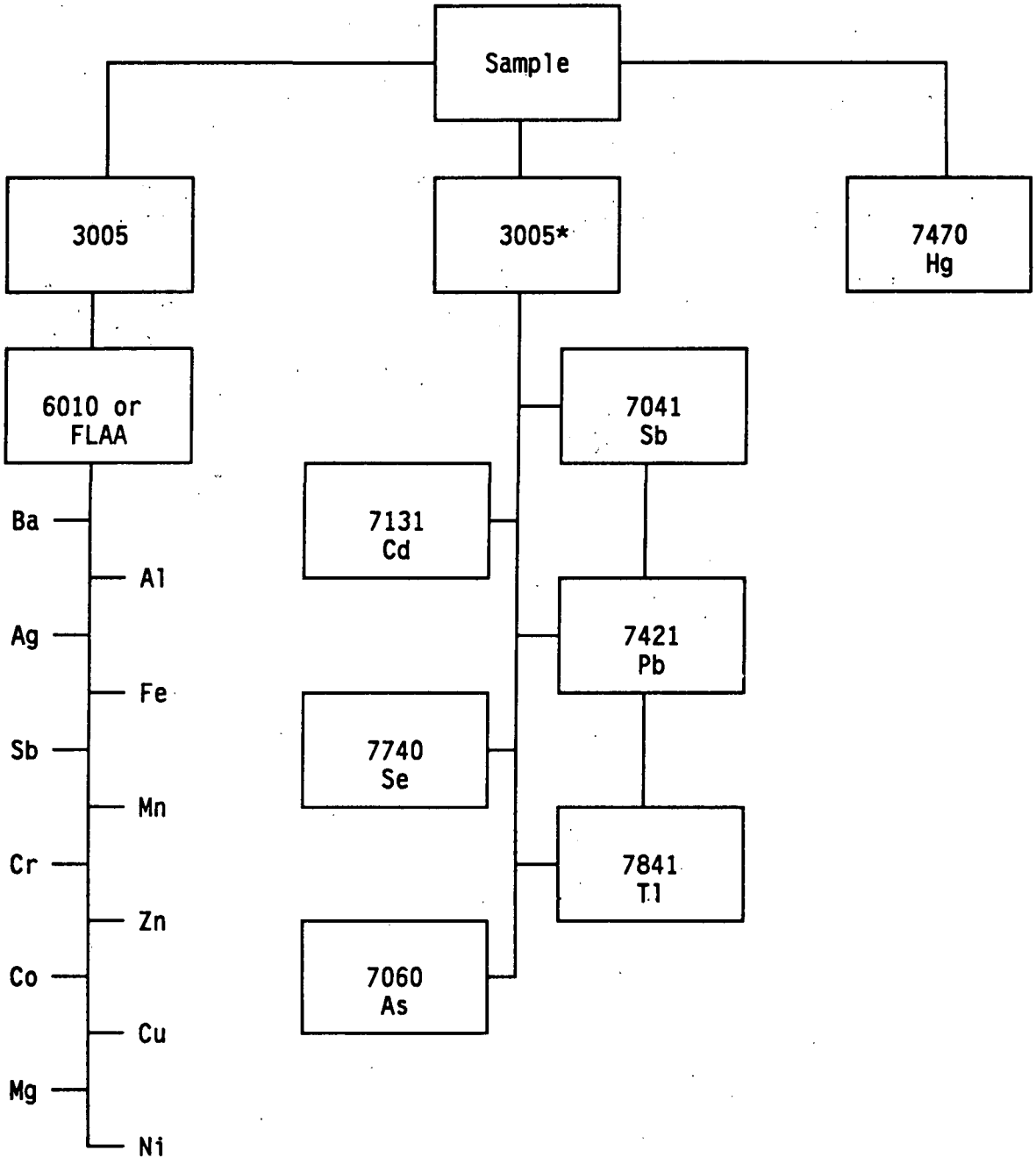
[1]Optional: Cleanup required only if interferences prevent analysis.

Figure 2-7A. Ground Water Analysis.



[1]Barcelona, 1984 (See Reference 1)
[2]Riggin, 1984 (See Reference 2)
[3]McKee, 1984 (See Reference 3)

Figure 2-7B. Indicator Analyte.



*Graphite Furnace Atomic Absorption is required to achieve detection limits.

Figure 2-7C. Ground Water.

2.6 REFERENCES

1. Barcelona, M.J., TOC Determinations in Ground Water, Ground Water 22(1), pp. 18-24 (1984).

2. Riggin, R., et al., Development and Evaluation of Methods for Total Organic Halide and Purgeable Organic Halide in Wastewater, Environmental Monitoring and Support Laboratory, Cincinnati, OH, EPA 600/4-84-008, 1984.

3. McKee, G., et al., Determination of Inorganic Anions in Water by Ion Chromatography, EPA 600/4-87-017 (Technical addition to Methods for Chemical Analysis of Water and Wastewater, EPA 600/4-79-020), Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1984.

Table 2-1: Phenols and Organic Acids

Benzoic acid
Benzyl alcohol
2-sec-Butyl-4,6-dinitrophenol (DNBP)
4-Chloro-3-methylphenol
2-Chlorophenol
Cresol (methyl phenols)
2-Cyclohexyl-4,6-dinitrophenol
2,4-Dichlorophenol
2,6-Dichlorophenol
2,4-Dimethylphenol
4,6-Dinitro-o-cresol
2,4-Dinitrophenol
2-Methyl-4,6-dinitrophenol
2-Nitrophenol
4-Nitrophenol
Pentachlorophenol
Phenol
Tetrachlorophenols
Trichlorophenols

Table 2-2: Phthalate Esters

Benzyl butyl phthalate
Bis(2-ethylhexyl)phthalate
Diethyl phthalate
Di-n-butyl phthalate
Dimethyl phthalate
Di-n-octyl phthalate

Table 2-3: Nitroaromatics and Cyclic Ketones

Dinitrobenzene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Isophorone
Naphthoquinone
Nitrobenzene

Table 2-4: Polyaromatic Hydrocarbons

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(j)fluoranthene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene
Chrysene
Dibenz(a,h)acridine
Dibenz(a,j)acridine
Dibenz(a,h)anthracene (Dibenzo(a,h)anthracene)
7H-Dibenzo(c,g)carbazole
Dibenzo(a,e)pyrene
Dibenzo(a,h)pyrene
Dibenzo(a,i)pyrene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
3-Methylcholanthrene
Naphthalene
Phenanthrene
Pyrene

Table 2-5: Chlorinated Hydrocarbons

Benzotrichloride
Benzyl chloride
2-Chloronaphthalene
Dichlorobenzenes
Dichloromethylbenzenes (Dichlorotoluenes)
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclohexane
Hexachlorocyclopentadiene
Hexachloroethane
Pentachlorohexane
Tetrachlorobenzenes
Trichlorobenzenes

Table 2-6: Base/Neutral

Acenaphthene
Acenaphthylene
Acetophenone
Aldrin
Aniline
Anthracene
4-Aminobiphenyl
Aroclor-1016
Aroclor-1221
Aroclor-1232
Aroclor-1242
Aroclor-1248
Aroclor-1254
Aroclor-1260
Benzidine
Benzo(a)anthracene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene
Benzo(a)pyrene
α-BHC
β-BHC
δ-BHC
γ-BHC
Bis(2-chloroethoxy)methane
Bis(2-chloroethyl)ether
Bis(2-chloroisopropyl)ether
Bis(2-ethylhexyl)phthalate
4-Bromophenyl phenyl ether
Butyl benzyl phthalate
Chlordane
4-Chloroaniline
1-Chloronaphthalene
2-Chloronaphthalene
4-Chlorophenyl phenyl ether
Chrysene
4,4'-DDD
4,4'-DDE
4,4'-DDT
Dibenz(a,j)acridine
Dibenz(a,h)anthracene
Dibenzofuran
Di-n-butyl phthalate
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2-Dichlorobenzene
3,3'-Dichlorobenzidine
Dieldrin
Diethyl phthalate
p-Dimethylaminoazobenzene
7,12-Dimethylbenz(a)anthracene
α-,α-Dimethylphethylamine
Dimethyl phthalate
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Diphenylamine
1,2-Diphenylhydrazine
Di-n-octyl phthalate
Endosulfan I
Endosulfan II
Endosulfan sulfate
Endrin
Endrin aldehyde
Endrin ketone
Ethyl methanesulfonate
Fluoranthene
Fluorene
2-Fluorobiphenyl
Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Indeno(1,2,3-cd)pyrene
Isphorone
Methoxychlor
3-Methylcholanthrene
Methyl methanesulfonate
2-Methylnaphthalene
Naphthalene
1-Naphthylamine
2-Naphthylamine
2-Nitroaniline
3-Nitroaniline
4-Nitroaniline
Nitrobenzene
N-Nitroso-di-n-butylamine
N-Nitrosodimethylamine
N-Nitrosodiphenylamine
N-Nitrosodipropylamine
N-Nitrosopiperidine
Pentachlorobenzene
Pentachloronitrobenzene
Phenacetin
Phenanthrene
2-Picoline
Pronamide
Pyrene
1,2,4,5-Tetrachlorobenzene
1,2,4-Trichlorobenzene
Toxaphene

Table 2-7: Organophosphorous Pesticides

Azinphos methyl
Bolstar (Sulprofos)
Chlorpyrifos
Coumaphos
Demeton
Diazinon
Dichlorvos
Dimethoate
Disulfoton
EPN
Ethoprop
Fensulfothion
Fenthion
Malathion
Merphos
Mevinphos
Monochrotophos
Naled
Parathion
Parathion methyl
Phorate
Ronnel
Stirophos (Tetrachlorvinphos)
Sulfotepp
TEPP
Tokuthion (Prothiofos)
Trichloronate

Table 2-8: Organochlorine Pesticides and PCB's

Aldrin
α-BHC
β-BHC
δ-BHC
γ-BHC (Lindane)
Chlordane
4,4'-DDD
4,4'-DDE
4,4'-DDT
Dieldrin
Endosulfan I
Endosulfan II
Endosulfan sulfate
Endrin
Endrin aldehyde
Heptachlor
Heptachlor epoxide
Kepone
Methoxychlor
Toxaphene
PCB-1016 (Aroclor-1016)
PCB-1221 (Aroclor-1221)
PCB-1232 (Aroclor-1232)
PCB-1242 (Aroclor-1242)
PCB-1248 (Aroclor-1248)
PCB-1254 (Aroclor-1254)
PCB-1260 (Aroclor-1260)

Table 2-9: Chlorinated Herbicides

2,4-D
2,4-DB
2,4,5-T
2,4,5-TP (Silvex)
Dalapon
Dicamba
Dichloroprop
Dinoseb
MCPA
MCPP

Table 2-10: Halogenated Volatiles

Benzyl chloride
Bis(2-chloroethoxy)methane
Bis(2-chloroisopropyl)ether
Bromobenzene
Bromodichloromethane
Bromoform
Bromomethane
Carbon tetrachloride
Chloracetaldehyde
Chloral
Chlorobenzene
Chloroethane
Chloroform
1-Chlorohexane
2-Chloroethyl vinyl ether
Chloromethane
Chloromethyl methyl ether
Chlorotoluene
Dibromochloromethane
Dibromomethane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethylene (Vinylidene chloride)
trans-1,2-Dichloroethylene
Dichloromethane
1,2-Dichloropropane
1,3-Dichloropropylene
1,1,2,2-Tetrachloroethane
1,1,1,2-Tetrachloroethane
Tetrachloroethylene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethylene
Trichlorofluoromethane
Trichloropropane
Vinyl chloride

Table 2-11: Non-halogenated Volatiles

Acrylamide
Diethyl ether
Ethanol
Methyl ethyl ketone (MEK)
Methyl isobutyl ketone (MIBK)
Paraldehyde (trimer of acetaldehyde)

Table 2-12: Aromatic Volatiles

Benzene
Chlorobenzene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Ethyl benzene
Toluene
Xylenes (Dimethyl benzenes)

Table 2-13: Acetonitrile, Acrolein, Acrylonitrile

Acetonitrile
Acrolein (Propenal)
Acrylonitrile

Table 2-14: Volatiles

Acetone
Acrolein
Acrylonitrile
Benzene
Bromochloromethane
Bromodichloromethane
4-Bromofluorobenzene
Bromoform
Bromomethane
2-Butanone (Methyl ethyl ketone)
Carbon disulfide
Carbon tetrachloride
Chlorobenzene
Chlorodibromomethane
Chloroethane
2-Chloroethyl vinyl ether
Chloroform
Chloromethane
Dibromomethane
1,4-Dichloro-2-butane
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
trans-1,2-Dichloroethene
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
1,4-Difluorobenzene
Ethanol
Ethylbenzene
Ethyl methacrylate
2-Hexanone
Iodomethane
Methylene chloride
4-Methyl-2-pentanone
Styrene
1,1,2,2-Tetrachloroethane
Toluene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Trichlorofluoromethane
1,2,3-Trichloropropane
Vinyl acetate
Vinyl chloride
Xylene

Table 2-15: Ground Water Monitoring Detection Limits

Analyte Class	Specific Analyte	Detection Limit (ug/L unless otherwise noted)
Volatile Organic Compounds		10 ug/L (nominal)
Semivolatile Base/Neutral Extractable Compounds		20 ug/L (nominal)
Semivolatile Acidic Extractable Compounds		20 ug/L (nominal)
Metals		
	Aluminum	200
	Antimony	60
	Arsenic	10
	Barium	200
	Beryllium	5
	Cadmium	2
	Calcium	5,000
	Chromium	10
	Cobalt	50
	Copper	25
	Iron	100
	Lead	5
	Magnesium	5,000
	Manganese	15
	Mercury	0.2
	Nickel	40
	Potassium	5,000
	Selenium	5
	Silver	10
	Sodium	5,000
	Thallium	10
	Vanadium	50
	Zinc	20

(continued on next page)

Table 2-15: Ground Water Monitoring Detection Limits (Continued)

Analyte Class	Specific Analyte	Detection Limit (ug/L unless otherwise noted)
Herbicides, by Method 8150 (capillary column optional)		
	Chlorobenzilate	60
	2,4-D	80
	2,4,5-TP	60
	2,4-DB	1.0
	2,4,5-T	200
	Sulfurous acid, 2-chloroethyl 2-[4-(1,1-dimethyl)-phenoxy]-1-methyl-ethyl ester	60
Dioxins and Dibenzofurans, by Method 8280		10 ppt per congener
Anions and Indicator Analyses		
	Bromide	1000
	Chloride	1000
	Cyanide	10
	Fluoride	1000
	NH_3	300
	Nitrate-N	300
	Nitrite-N	300
	Phenolics	50
	POC	10
	POX	5
	Sulfate	1000
	Sulfide	1000
	TOC	1000
	TOX	5

TABLE 2-16. REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

Name	Container[1]	Preservation	Maximum holding time
Bacterial Tests:			
Coliform, fecal and total	P, G	Cool, 4°C, 0.008% $Na_2S_2O_3$	6 hours
Fecal streptococci	P, G	Cool, 4°C, 0.008% $Na_2S_2O_3$	6 hours
Inorganic Tests:			
Acidity	P, G	Cool, 4°C	14 days
Alkalinity	P, G	Cool, 4°C	14 days
Ammonia	P, G	Cool, 4°C, H_2SO_4 to pH<2	28 days
Biochemical oxygen demand	P, G	Cool, 4°C	48 hours
Bromide	P, G	None required	28 days
Biochemical oxygen demand, carbonaceous	P, G	Cool, 4°C	48 hours
Chemical oxygen demand	P, G	Cool, 4°C, H_2SO_4 to pH<2	28 days
Chloride	P, G	None required	28 days
Chlorine, total residual	P, G	None required	Analyze immediately
Color	P, G	Cool, 4°C	48 hours
Cyanide, total and amenable to chlorination	P, G	Cool, 4°C, NaOH to pH>12, 0.6g ascorbic acid	14 days
Fluoride	P	None required	28 days
Hardness	P, G	HNO_3 to pH<2, H_2SO_4 to pH<2	6 months
Hydrogen ion (pH)	P, G	None required	Analyze immediately
Kjeldahl and organic nitrogen	P, G	Cool, 4°C, H_2SO_4 to pH<2	28 days
Metals:			
Chromium VI	P, G	Cool, 4°C	24 hours
Mercury	P, G	HNO_3 to pH<2	28 days
Metals, except chromium VI and mercury	P, G	HNO_3 to pH<2	6 months
Nitrate	P, G	Cool, 4°C	48 hours
Nitrate-nitrite	P, G	Cool, 4°C, H_2SO_4 to pH<2	28 days
Nitrite	P, G	Cool, 4°C	48 hours
Oil and grease	G	Cool, 4°C, H_2SO_4 to pH<2	28 days
Organic carbon	P, G	Cool, 4°C, HCl or H_2SO_4 to pH<2	28 days
Orthophosphate	P, G	Filter immediately, cool, 4°C	48 hours
Oxygen, Dissolved Probe	G Bottle and top	None required	Analyze immediately
Winkler	do	Fix on site and store in dark	8 hours
Phenols	G only	Cool, 4°C, H_2SO_4 to pH<2	28 days
Phosphorus (elemental)	G	Cool, 4°C	48 hours
Phosphorus, total	P, G	Cool, 4°C, H_2SO_4 to pH<2	28 days
Residue, total	P, G	Cool, 4°C	7 days
Residue, Filterable	P, G	Cool, 4°C	7 days
Residue, Nonfilterable (TSS)	P, G	Cool, 4°C	7 days
Residue, Settleable	P, G	Cool, 4°C	48 hours
Residue, volatile	P, G	Cool, 4°C	7 days
Silica	P	Cool, 4°C	28 days
Specific conductance	P, G	Cool, 4°C	28 days

TABLE 2-16. REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES (CONTINUED)

Name	Container[1]	Preservation	Maximum holding time
Sulfate	P, G	Cool, 4°C	28 days
Sulfide	P, G	Cool, 4°C, add zinc acetate plus sodium hydroxide to pH>9	7 days
Sulfite	P, G	None required	Analyze immediately
Surfactants	P, G	Cool, 4°C	48 hours
Temperature	P, G	None required	Analyze
Turbidity	P, G	Cool, 4°C	48 hours
Organic Tests:			
Purgeable Halocarbons	G, Teflon-lined septum	Cool, 4°C, 0.008% $Na_2S_2O_3$	14 days
Purgeable aromatic hydrocarbons	G, Teflon-lined septum	Cool, 4°C, 0.008% $Na_2S_2O_3$, HCl to pH2	14 days
Acrolein and acrylonitrile	G, Teflon-lined septum	Cool, 4°C, 0.008% $Na_2S_2O_3$, Adjust pH to 4-5	14 days
Phenols	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$	7 days until extraction, 40 days after extraction
Benzidines	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$	7 days until extraction
Phthalate esters	G, Teflon-lined cap	Cool, 4°C	7 days until extraction 40 days after extraction
Nitrosamines	G, Teflon-lined cap	Cool, 4°C, store in dark, 0.008% $Na_2S_2O_3$	40 days after extraction
PCBs, acrylonitrile	G, Teflon-lined cap	Cool, 4°C	40 days after extraction
Nitroaromatics and isophorone	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$ store in dark	40 days after extraction
Polynuclear aromatic hydrocarbons	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$ store in dark	40 days after extraction
Haloethers	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$	40 days after extraction
Chlorinated hydrocarbons	G, Teflon-lined cap	Cool, 4°C	40 days after extraction
TCDD	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$	40 days after extraction
Total organic halogens	G, Teflon-lined cap	Cool, 4°C, H_2SO_4 to pH<2	7 days
Pesticides Tests:			
Pesticides	G, Teflon-lined cap	Cool, 4°C, pH 5-9	40 days after extraction
Radiological Tests:			
Alpha, beta and radium	P, G	HNO_3 to pH<2	6 months

[1]Polyethylene (P) or Glass (G)

CHAPTER THREE

METALLIC ANALYTES

3.1 SAMPLING CONSIDERATIONS

3.1.1 Introduction

This manual contains procedures for the analysis of metals in a variety of matrices. These methods are written as specific steps in the overall analysis scheme -- sample handling and preservation, sample digestion or preparation, and sample analysis for specific metal components. From these methods, the analyst must assemble a total analytical protocol which is appropriate for the sample to be analyzed and for the information required. This introduction discusses the options available in general terms, provides background information on the analytical techniques, and highlights some of the considerations to be made when selecting a total analysis protocol.

3.1.2 Definition of Terms

Optimum concentration range: A range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating conditions employed.

Sensitivity: a) Atomic Absorption: The concentration in milligrams of metal per liter that produces an absorption of 1%; b) ICP: The slope of the analytical curve, i.e., the functional relationship between emission intensity and concentration.

Method detection limit (MDL): The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined from analysis of a sample in a given matrix containing analyte which has been processed through the preparative procedure.

Total recoverable metals: The concentration of metals in an unfiltered sample following treatment with hot dilute mineral acid (Method 3005).

Dissolved metals: The concentration of metals determined in sample after the sample is filtered through a 0.45-um filter (Method 3005).

Suspended metals: The concentration of metals determined in the portion of a sample that is retained by a 0.45-um filter (Method 3005).

Total metals: The concentration of metals determined in a sample following digestion by Methods 3010, 3020, or 3050.

Instrument detection limit: The concentration equivalent to a signal due to the analyte which is equal to three times the standard deviation of a series of 7 replicate measurements of a reagent blank's signal at the same wavelength.

Interference check sample (ICP): A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors.

Initial calibration verification standard: A certified (EPA or other) or independently prepared solution used to verify the accuracy of the initial calibration. For ICP analysis, it must be run at each wavelength used in the analysis.

Continuing calibration verification: Used to assure calibration accuracy during each analysis run. It must be run for each analyte at a frequency of 10% or every 2 hrs during the run, whichever is more frequent. It must also be analyzed at the beginning of the run and after the last analytical sample. Its concentration must be at or near the mid-range levels of the calibration curve.

Calibration standards: A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve).

Linear dynamic range: The concentration range over which the analytical curve remains linear.

Preparation blank: A volume of Type II water processed through each sample preparation procedure.

Calibration blank: A volume of Type II water acidified with the same amounts of acids as were the standards and samples.

Laboratory control standard: A volume of Type II water spiked with known concentrations of analytes and carried through the preparation and analysis procedure as a sample. It is used to monitor loss/recovery values.

Method of standard addition: The standard-addition technique involves the use of the unknown and the unknown plus a known amount of standard. See Method 7000, Section 8.7 for detailed instructions.

Sample holding time: The storage time allowed between sample collection and sample analysis when the designated preservation and storage techniques are employed.

3.1.3 Sample Handling and Preservation

Sample holding times, digestion procedure and suggested collection volumes are listed in Table 1. The sample volumes required depend upon the number of different digestion procedures necessary for analysis. This may be TABLE 1.

AND RECOMMENDED COLLECTION VOLUMES FOR METAL DETERMINATIONS

Measurement	Digestion Vol. Req.[a] (mL)	Collection Volume (mL)[b]	Preservative	Holding Time
Metals (except hexavalent chromium and mercury):				
Total recoverable	100	600	HNO_3 to pH <2	6 mo
Dissolved	100	600	Filter on site; HNO_3 to pH <2	6 mo
Suspended	100	600	Filter on site	6 mo
Total	100	600	HNO_3 to pH <2	6 mo
Chromium VI:	100	400	Cool, 4°C	24 hr
Mercury:				
Total	100	400	HNO_3 to pH <2	28 days
Dissolved	100	400	Filter; HNO_3 to pH <2	28 days

[a]Solid samples must be at least 200 g and usually require no preservation other than storing at 4°C until analyzed.

[b]Either plastic or glass containers may be used.

determined by the application of graphite-furnace atomic absorption spectrometry (GFAA), flame atomic absorption spectrometry (FLAA), inductively coupled argon plasma emission spectrometry (ICP), hydride-generation atomic absorption spectrometry (HGAA), or cold-vapor atomic absorption spectrometry (CVAA) techniques, each of which may require different digestion procedures. The indicated volumes in Table 1 refer to that required for the individual digestion procedures and recommended sample collection volumes.

In the determination of trace metals, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption, and (b) depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis require particular attention. The

following cleaning treatment sequence has been determined to be adequate to minimize contamination in the sample bottle, whether borosilicate glass, linear polyethylene, polypropylene, or Teflon: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and Type II water.

NOTE: **Chromic acid should not be used to clean glassware**, especially if chromium is to be included in the analytical scheme. Commercial, non-chromate products (e.g., Nochromix) may be used in place of chromic acid if adequate cleaning is documented by an analytical quality control program. (Chromic acid should also not be used with plastic bottles.)

3.1.4 Safety

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data-handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available. They are:

1. "Carcinogens - Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

2. "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, revised January 1976.

3. "Proposed OSHA Safety and Health Standards, Laboratories," Occupational Safety and Health Administration, Federal Register, July 24, 1986, p. 26660.

4. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd edition, 1979.

3.2 SAMPLE PREPARATION METHODS

The methods in SW-846 for sample digestion or preparation are as follows:

Method 3005 prepares ground water and surface water samples for total recoverable and dissolved metals determination by FLAA or ICP. The unfiltered or filtered sample is heated with dilute HCl and HNO_3 prior to metal determination.

Method 3010 prepares waste samples for total metal determination by FLAA and ICP. The samples are vigorously digested with nitric acid followed by dilution with hydrochloric acid. The method is applicable to aqueous samples, EP and mobility-procedure extracts.

Method 3020 prepares waste samples for total metals determination by furnace GFAA. The samples are vigorously digested with nitric acid followed by dilution with nitric acid. The method is applicable to aqueous samples, EP and mobility-procedure extracts.

Method 3040 prepares oily waste samples for soluble metals determination by AA and ICP methods. The samples are dissolved and diluted in organic solvent prior to analysis. The method is applicable to the organic extract in the oily waste EP procedure and other samples high in oil, grease, or wax content.

Method 3050 prepares waste samples for total metals determination by AA and ICP. The samples are vigorously digested in nitric acid and hydrogen peroxide followed by dilution with either nitric or hydrochloric acid. The method is applicable to soils, sludges, and solid waste samples.

METHOD 3005

ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR DISSOLVED METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 Method 3005 is an acid digestion procedure used to prepare surface water and ground water samples for analysis by flame atomic absorption spectroscopy (FAA) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3005 may be analyzed by AAS or ICP for the following metals:

Aluminum	Magnesium
Antimony	Manganese
Arsenic*	Molybdenum
Barium	Nickel
Beryllium	Potassium
Cadmium	Selenium*
Calcium	Silver
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

*ICP only

1.2 For the analysis of total dissolved metals, the sample is filtered at the time of collection, prior to acidification with nitric acid.

2.0 SUMMARY OF METHOD

2.1 Total recoverable metals: The entire sample is acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is filtered and diluted to volume, and is then ready for analysis.

2.2 Dissolved metals: The sample is filtered through a 0.5 um filter at the time of collection and the liquid phase is then acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is again filtered (if necessary) and diluted to volume and is then ready for analysis.

3.0 INTERFERENCES

3.1 The analyst should be cautioned that this digestion procedure may not be sufficiently vigorous to destroy some metal complexes.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers of assorted sizes.

4.2 Watch glasses.

4.3 Qualitative filter paper and filter funnels.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid, reagent grade (HNO_3): Acid should be analyzed to determine level of impurities. If method blank is <MDL, then acid can be used.

5.3 Concentrated hydrochloric acid, reagent grade (HCl): Acid should be analyzed to determine level of impurities. If method blank is <MDL, then acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Sampling:

6.3.1 **Total recoverable metals:** All samples must be acidified at the time of collection with HNO_3 (5 mL/L).

6.3.2 **Dissolved metals:** All samples must be filtered through a 0.5 um filter and then acidified at the time of collection with HNO_3 (5 mL/L).

7.0 PROCEDURE

7.1 Transfer a 100-mL aliquot of well-mixed sample to a beaker.

7.2 For metals that are to be analyzed by FLAA or ICP, add 2 mL of concentrated HNO_3 and 5 mL of concentrated HCl. The sample is covered with a ribbed watch glass and heated on a steam bath or hot plate at 90 to 95°C until the volume has been reduced to 15-20 mL.

CAUTION: Do not boil. Antimony is easily lost by volatilization from hydrochloric acid media.

7.3 Remove the beaker and allow to cool. Wash down the beaker walls and watch glass with Type II water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer; this additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO_3.

7.4 Adjust the final volume to 100 mL with Type II water.

8.0 QUALITY CONTROL

8.1 For each analytical batch of samples processed, blanks (Type II water and reagents) should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analytical process. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 20% is recommended.

8.3 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

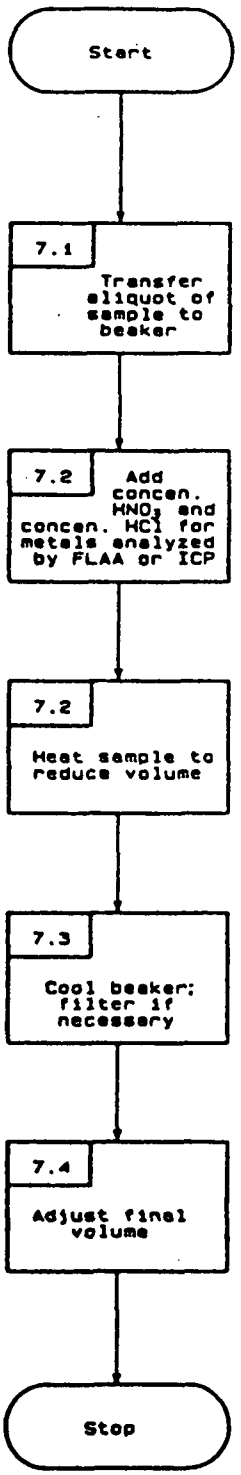
9.1 No data provided.

10.0 REFERENCES

10.1 None required.

METHOD 3005

ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR DISSOLVED METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY



METHOD 3010

ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS FOR TOTAL METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis, by FLAA or ICP, for the metals listed below. The procedure is used to determine total metals.

1.2 Samples prepared by Method 3010 may be analyzed by FLAA or ICP for the following:

Aluminum	Lead
Arsenic	Magnesium
Barium	Manganese
Beryllium	Molybdenum
Cadmium	Nickel
Calcium	Potassium
Chromium	Selenium
Cobalt	Sodium
Copper	Thallium
Iron	Vanadium
	Zinc

NOTE: See Method 7760 for FLAA preparation for Silver.

1.3 This digestion procedure is not suitable for samples which will be analyzed by graphite furnace atomic absorption spectroscopy because hydrochloric acid can cause interferences during furnace atomization.

2.0 SUMMARY OF METHOD

2.1 A mixture of HNO_3 and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of HNO_3 until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is refluxed with HCl and brought up to volume. If sample should go to dryness, it must be discarded and the sample reprepared.

3.0 INTERFERENCES

3.1 Interferences are discussed in the referring analytical method.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers: 150-mL.
4.2 Watch glasses: Ribbed and plain.
4.3 Qualitative filter paper or centrifugation equipment.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid, reagent grade (HNO_3): Acid should be analyzed to determine levels of impurities. If method blank is <MDL, the acid can be used.

5.3 Hydrochloric acid, reagent grade (1:1 HCl): Prepared from Type II water and hydrochloric acid. Hydrochloric acid should be analyzed to determine level of impurities. If method blank is <MDL, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable. See Chapter Three, Section 3.1.3, for further information.

6.3 Aqueous wastewaters must be acidified to a pH of <2 with HNO_3.

6.4 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Transfer a 100-mL representative aliquot of the well-mixed sample to a 150-mL Griffin beaker and add 3 mL of concentrated HNO_3. Cover the beaker with a ribbed watch glass. Place the beaker on a hot plate and cautiously evaporate to a low volume (5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3-mL portion of concentrated HNO_3. Re-cover the beaker with a nonribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If a sample is allowed to go to dryness, low recoveries will result. Should this occur, discard the sample and reprepare.

7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, uncover the beaker or use a ribbed watch glass, and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the beaker to go dry. Cool the beaker. Add a small quantity of 1:1 HCl (10 mL/100 mL of final solution) and warm the beaker for an additional 15 min to dissolve any precipitate or residue resulting from evaporation.

7.3 Wash down the beaker walls and watch glass with Type II water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO_3. Adjust to the final volume of 100 mL with Type II water. The sample is now ready for analysis.

8.0 QUALITY CONTROL

8.1 For each analytical batch of samples processed, blanks (Type II water and reagents) should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analytical process. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 20% is recommended.

8.3 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

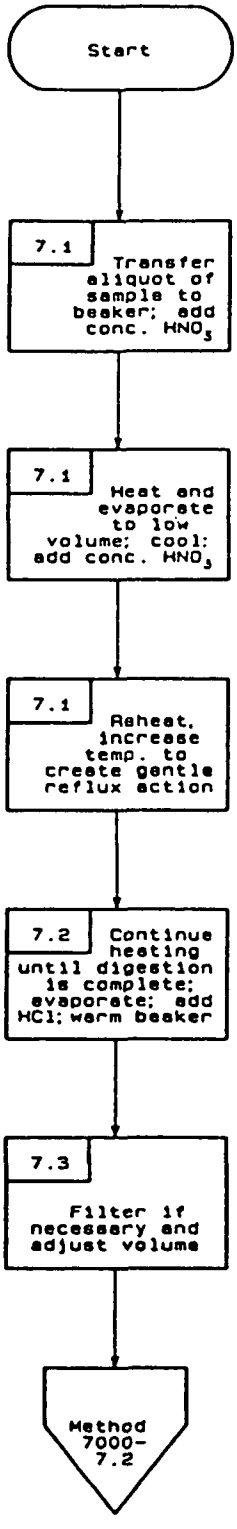
8.4 The method of standard addition shall be used for the analysis of all EP extracts (see Method 7000, Section 8.7).

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

10.1 None required.


Start
7.1
Transfer aliquot of sample to beaker; add conc. HNO_3
7.1
Heat and evaporate to low volume; cool; add conc. HNO_3
7.1
Reheat, increase temp. to create gentle reflux action
7.2
Continue heating until digestion is complete; evaporate; add HCl; warm beaker
7.3
Filter if necessary and adjust volume
Method 7000-7.2

METHOD 3020

ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS
FOR TOTAL METALS FOR ANALYSIS BY GFAA SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for analysis by furnace atomic absorption spectroscopy (GFAA) for the metals listed below. The procedure is used to determine the total amount of the metal in the sample.

1.2 Samples prepared by Method 3020 may be analyzed by GFAA for the following metals:

Beryllium	Lead
Cadmium	Molybdenum
Chromium	Thallium
Cobalt	Vanadium

NOTE: For the digestion and GFAA analysis of arsenic and selenium, see Methods 3050, 7060, and 7740. For digestion and GFAA analysis of silver, see Method 7761.

2.0 SUMMARY OF METHOD

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is cooled and brought up in dilute nitric acid such that the final dilution contains 3% (v/v) HNO_3. If the sample contains suspended solids, it must be centrifuged, filtered, or allowed to settle.

3.0 INTERFERENCES

3.1 Interferences are discussed in the referring analytical method.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers: 150-mL.
4.2 Watch glasses.
4.3 Qualitative filter paper or centrifugation equipment.

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5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid, reagent grade (HNO_3): Acid should be analyzed to determine levels of impurities. If method blank is <MDL, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable. See Chapter Three, Section 3.1.3, for further information.

6.3 Aqueous wastewaters must be acidified to a pH of <2 with HNO_3.

6.4 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Transfer a 100-mL representative aliquot of the well-mixed sample to a 150-mL Griffin beaker and add 3 mL of concentrated HNO_3. Cover the beaker with a ribbed watch glass. Place the beaker on a hot plate and cautiously evaporate to a low volume (5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3-mL portion of concentrated HNO_3. Re-cover the beaker with a non-ribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). When the digestion is complete, evaporate to a low volume (3 mL); use a ribbed watch glass, not allowing any portion of the bottom of the beaker to go dry. Remove the beaker and add approximately 10 mL of Type II water, mix, and continue warming the beaker for 10 to 15 min to allow additional solubilization of any residue to occur.

7.3 Remove the beaker from the hot plate and wash down the beaker walls and watch glass with Type II water. When necessary, filter or centrifuge the sample to remove silicates and other insoluble material that may interfere

with injecting the sample into the graphite atomizer. (This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO_3.) Adjust to the final volume of 100 mL with Type II water. The sample is now ready for analysis.

8.0 QUALITY CONTROL

8.1 For each group of samples processed, preparation blanks (Type II water and reagents) should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 20% is recommended.

8.3 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

8.4 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

8.5 The method of standard addition shall be used for the analysis of all EP extracts. See Method 7000, Section 8.7, for further information.

9.0 METHOD PERFORMANCE

9.1 No data provided.

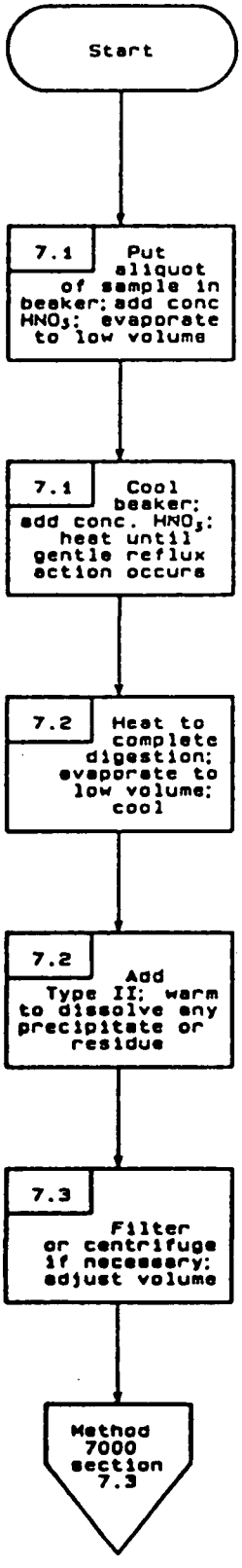
10.0 REFERENCES

10.1 None required.

METHOD 3020

ACID DIGESTION FOR AQUEOUS SAMPLES AND EXTRACTS

FOR TOTAL METALS FOR ANALYSIS BY GFAA SPECTROSCOPY



Revision 0
Date September 1986

METHOD 3040

DISSOLUTION PROCEDURE FOR OILS, GREASES, OR WAXES

1.0 SCOPE AND APPLICATION

1.1 Method 3040 is used for the preparation of samples containing oils, greases, or waxes for analysis by atomic absorption spectroscopy (AAS) or inductively coupled argon plasma emission spectroscopy (ICP) for the following metals:

Antimony	Iron
Beryllium	Manganese
Cadmium	Nickel
Chromium	Vanadium
Copper	

1.2 This method is a solvent dissolution procedure, not a digestion procedure. This procedure can be very useful in the analysis of crude oil, but with spent or used oil high in particulate material it is less effective; most particulate material is not dissolved, and therefore the analysis is not a "total" metal determination. Because the highest percentage of metals is expected to be contained in the particulate material, oil analysis using Method 3040 will not provide an adequate estimate of the total metals concentration.

2.0 SUMMARY OF METHOD

2.1 A representative sample is dissolved in an appropriate solvent (e.g., xylene or methyl isobutyl ketone). Organometallic standards are prepared using the same solvent, and the samples and standards are analyzed by AAS or ICP.

3.0 INTERFERENCES

3.1 Diluted samples and diluted organometallic standards are often unstable. Once standards and samples are diluted, they should be analyzed as soon as possible.

3.2 Solvent blanks should be used to rinse nebulizers thoroughly following aspiration of high concentration standards or samples.

3.3 Viscosity differences can result in different rates of sample introduction; therefore, all analyses shall be performed by the method of standard addition. Peristaltic pumps often prove useful when analysis is performed by ICP.

4.0 APPARATUS AND MATERIALS

4.1 Volumetric glassware.

4.2 Balance.

4.3 Atomic absorption spectrometer: With an auxiliary oxidant control and a mechanism for background correction.

4.4 Inductively coupled argon plasma emission spectrometer system: With a mechanism for background correction and interelement interference correction. A peristaltic pump is optional.

5.0 REAGENTS

5.1 Methyl isobutyl ketone (MIBK).

5.2 Xylene.

5.3 Organometallic standards (two possible sources are Conostan Division, Conoco Speciality Products, Inc., P.O. Box 1267, Ponca City, OK 74601, and the U.S. Department of Commerce, National Bureau of Standards, Washington, DC 20234).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples shall be stored in an undiluted state at room temperature.

6.3 Samples should be processed and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Weigh out a 2-g representative sample of the waste or extract. Separate and weigh the phases if more than one phase is present.

7.2 Weigh an aliquot of the organic phase and dilute the aliquot in the appropriate solvent. Warming facilitates the subsampling of crude-type oils and greases and wax-type wastes. Xylene is usually the preferred solvent for longer-chain hydrocarbons and for most analyses performed by ICP. The longer-chain hydrocarbons usually require a minimum of a 1:10 dilution, and lighter oils may require only a 1:5 dilution if low detection limits are required.

7.3 All metals must be analyzed by the method of standard additions. Because the method of standard additions can account only for multiplicative interferences (matrix or physical interferences), the analytical program must

account for additive interference (nonspecific absorption and scattering in AAS and nonspecific emission and interelement interference in ICP) by employing background correction.

7.4 Sample preparation for the method of standard additions can be performed on a weight or volume basis. Sample aliquots of viscous wastes should be weighed. Weigh identical amounts of the sample into three wide-mouth vials. Dilute the first vial such that the final concentration falls on the lower end of the linear portion of the calibration curve and significantly above the detection limit. Add sufficient standard to the second aliquot to increase the sample concentration by approximately 50%. Adjust the third sample concentration so that it is approximately twice that of the first. The second and third aliquots are then diluted to the same final volume as the first aliquot.

7.5 Set up and calibrate the analytical instrumentation according to the manufacturer's directions for nonaqueous samples.

7.6 Report data as the weighted average for all sample phases.

8.0 QUALITY CONTROL

8.1 Preparation blanks (e.g., Conostan base oil or mineral oil plus reagents) should be carried through the complete sample-preparation and analytical process on a routine basis. These blanks will be useful in detecting and determining the magnitude of any sample contamination.

8.2 Duplicate samples should be processed on a routine basis. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 20% is recommended.

8.3 Samples and standards should be diluted as closely as possible to the time of analysis.

8.4 All analyses must be performed by the method of standard additions. See Method 7000, Section 8.7, for further information.

8.5 Data must be corrected for background absorption and emission and interelement interferences.

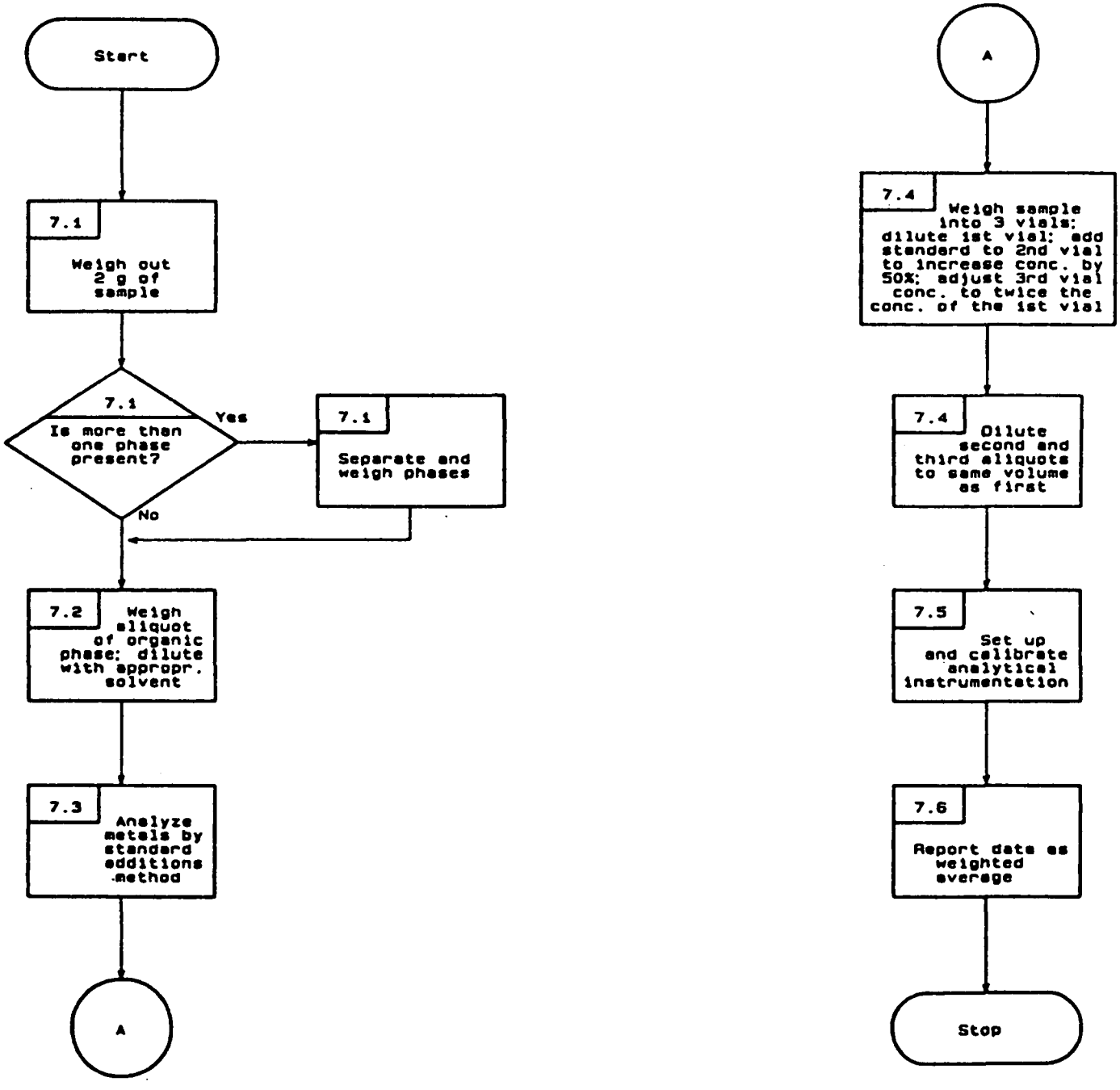
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

10.1 None required.

DISSOLUTION PROCEDURE FOR OILS, GREASE, OR WAXES



METHOD 3050

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

1.0 SCOPE AND APPLICATION

1.1 This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (FLAA and GFAA, respectively) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by ICP for all the listed metals, or by FLAA or GFAA as indicated below (see also Paragraph 2.1):

FLAA		GFAA
Aluminum	Magnesium	Arsenic
Barium	Manganese	Beryllium
Beryllium	Molybdenum	Cadmium
Cadmium	Nickel	Chromium
Calcium	Potassium	Cobalt
Chromium	Sodium	Iron
Cobalt	Thallium	Molybdenum
Copper	Vanadium	Selenium
Iron	Zinc	Thallium
Lead		Vanadium

2.0 SUMMARY OF METHOD

2.1 A representative 1- to 2-g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Dilute hydrochloric acid is used as the final reflux acid for (1) the ICP analysis of As and Se, and (2) the flame AA or ICP analysis of Al, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Mo, Pb, Ni, K, Na, Tl, V, and Zn. Dilute nitric acid is employed as the final dilution acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Pb, Mo, Se, Tl, and V. A separate sample shall be dried for a total solids determination.

3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050 is applicable to a given waste.

4.0 APPARATUS AND MATERIALS

4.1 Conical Phillips beakers: 250-mL.
4.2 Watch glasses.
4.3 Drying ovens: That can be maintained at 30°C.
4.4 Thermometer: That covers range of 0 to 200°C.
4.5 Whatman No. 41 filter paper (or equivalent).
4.6 Centrifuge and centrifuge tubes.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid, reagent grade (HNO_3): Acid should be analyzed to determine level of impurities. If method blank is <MDL, the acid can be used.

5.3 Concentrated hydrochloric acid, reagent grade (HCl): Acid should be analyzed to determine level of impurities. If method blank is <MDL, the acid can be used.

5.4 Hydrogen peroxide (30%) (H_2O_2): Oxidant should be analyzed to determine level of impurities.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable. See Chapter Three, Section 3.1.3, for further information.

6.3 Nonaqeuous samples shall be refrigerated upon receipt and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh to the nearest 0.01 g and transfer to a conical beaker a 1.00- to 2.00-g portion of sample.

7.2 Add 10 mL of 1:1 HNO_3, mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 to 15 min without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the watch glass, and reflux for 30 min. Repeat this last step to ensure complete oxidation.

Using a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.

7.3 After Step 7.2 has been completed and the sample has cooled, add 2 mL of Type II water and 3 mL of 30% H_2O_2. Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker.

7.4 Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.
NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

7.5 If the sample is being prepared for (a) the ICP analysis of As and Se, or (b) the flame AA or ICP analysis of Al, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Tl, V, and Zn, then add 5 mL of concentrated HCl and 10 mL of Type II water, return the covered beaker to the hot plate, and reflux for an additional 15 min without boiling. After cooling, dilute to 100 mL with Type II water. Particulates in the digestate that may clog the nebulizer should be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.5.1 **Filtration:** Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with Type II water.

7.5.2 **Centrifugation:** Centrifugation at 2,000-3,000 rpm for 10 min is usually sufficient to clear the supernatant.

7.5.3 The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO_3. The sample is now ready for analysis.

7.6 If the sample is being prepared for the furnace analysis of As, Be, Cd, Cr, Co, Pb, Mo, Se, Tl, and V, cover the sample with a ribbed watch glass and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL. After cooling, dilute to 100 mL with Type II water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.6.1 **Filtration:** Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with Type II water.

7.6.2 **Centrifugation:** Centrifugation at 2,000-3,000 for 10 min is usually sufficient to clear the supernatant.

7.6.3 The diluted digestate solution contains approximately 5% (v/v) HNO_3. For analysis, withdraw aliquots of appropriate volume and add any required reagent or matrix modifier. The sample is now ready for analysis.

7.7 Calculations:

7.7.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

7.7.2 If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

8.0 QUALITY CONTROL

8.1 For each group of samples processed, preparation blanks (Type II water and reagents) should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 20% is recommended.

8.3 Spiked samples or standard reference materials must be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

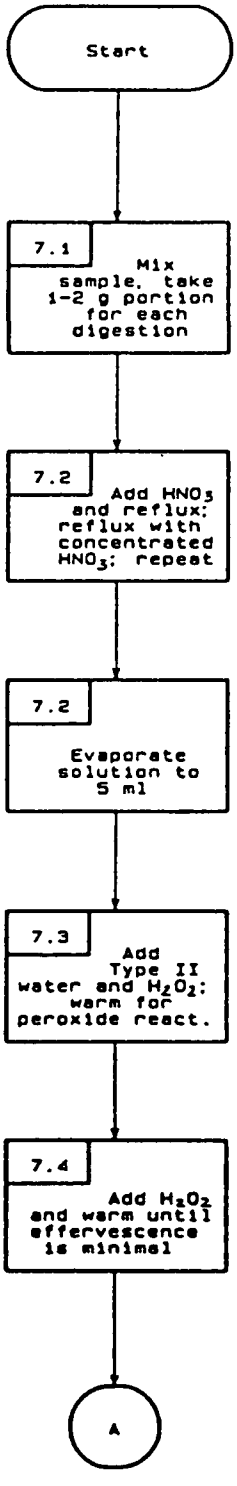
8.4 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

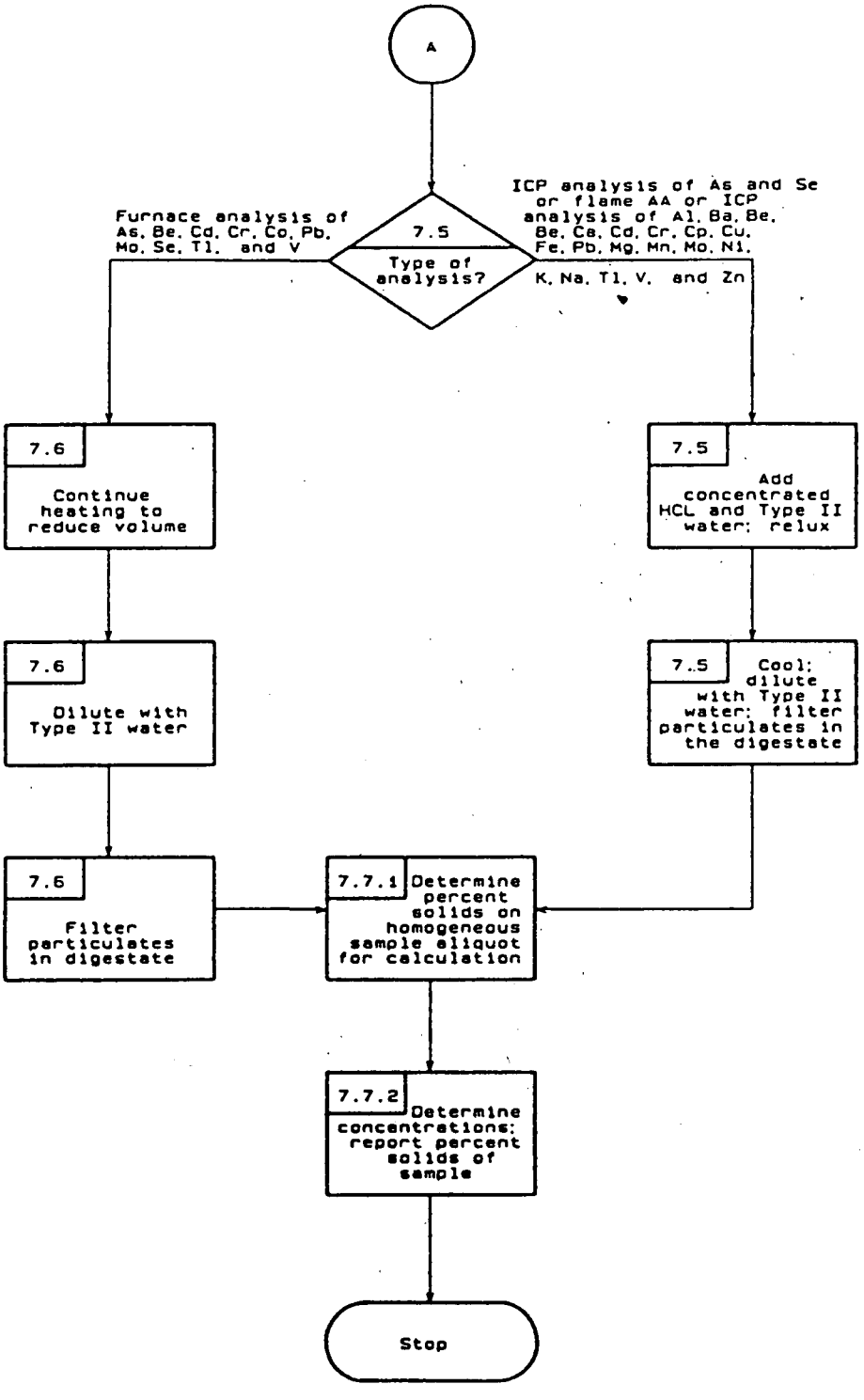
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

10.1 None required.


Start
7.1
Mix sample, take 1-2 g portion for each digestion
7.2
Add HNO_3 and reflux; reflux with concentrated HNO_3; repeat
7.2
Evaporate solution to 5 ml
7.3
Add Type II water and H_2O_2; warm for peroxide react.
7.4
Add H_2O_2 and warm until effervescence is minimal
A


A
7.5
Type of analysis?
Furnace analysis of As, Be, Cd, Cr, Co, Pb, Mo, Se, Tl, and V
ICP analysis of As and Se or flame AA or ICP analysis of Al, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Tl, V, and Zn
7.6
Continue heating to reduce volume
7.5
Add concentrated HCL and Type II water; relux
7.6
Dilute with Type II water
7.5
Cool; dilute with Type II water; filter particulates in the digestate
7.6
Filter particulates in digestate
7.7.1
Determine percent solids on homogeneous sample aliquot for calculation
7.7.2
Determine concentrations; report percent solids of sample
Stop

3.3 METHODS FOR DETERMINATION OF METALS

This manual contains six analytical techniques for trace metal determinations: inductively coupled argon plasma emission spectrometry (ICP), direct-aspiration or flame atomic absorption spectrometry (FAA), graphite-furnace atomic absorption spectrometry (GFAA), hydride-generation atomic absorption spectrometry (HGAA), cold-vapor atomic absorption spectrometry (CVAA), and several procedures for hexavalent chromium analysis. Each of these is briefly discussed below in terms of advantages, disadvantages, and cautions for analysis of wastes.

ICP's primary advantage is that it allows simultaneous or rapid sequential determination of many elements in a short time. The primary disadvantage of ICP is background radiation from other elements and the plasma gases. Although all ICP instruments utilize high-resolution optics and background correction to minimize these interferences, analysis for traces of metals in the presence of a large excess of a single metal is difficult. Examples would be traces of metals in an alloy or traces of metals in a limed (high calcium) waste. ICP and Flame AA have comparable detection limits (within a factor of 4) except that ICP exhibits greater sensitivity for refractories (Al, Ba, etc.). Furnace AA, in general, will exhibit lower detection limits than either ICP or FLAA.

Flame AAS (FLAA) determinations, as opposed to ICP, are normally completed as single element analyses and are relatively free of interelement spectral interferences. Either a nitrous-oxide/acetylene or air/acetylene flame is used as an energy source for dissociating the aspirated sample into the free atomic state making analyte atoms available for absorption of light. In the analysis of some elements the temperature or type of flame used is critical. If the proper flame and analytical conditions are not used, chemical and ionization interferences can occur.

Graphite Furnace AAS (GFAA) replaces the flame with an electrically heated graphite furnace. The furnace allows for gradual heating of the sample aliquot in several stages. Thus, the processes of desolvation, drying, decomposition of organic and inorganic molecules and salts, and formation of atoms which must occur in a flame or ICP in a few milliseconds may be allowed to occur over a much longer time period and at controlled temperatures in the furnace. This allows an experienced analyst to remove unwanted matrix components by using temperature programming and/or matrix modifiers. The major advantage of this technique is that it affords extremely low detection limits. It is the easiest to perform on relatively clean samples. Because this technique is so sensitive, interferences can be a real problem; finding the optimum combination of digestion, heating times and temperatures, and matrix modifiers can be a challenge for complex matrices.

Hydride AA utilizes a chemical reduction to reduce and separate arsenic or selenium selectively from a sample digestate. The technique therefore has the advantage of being able to isolate these two elements from complex samples which may cause interferences for other analytical procedures. Significant interferences have been reported when any of the following is present: 1) easily reduced metals (Cu, Ag, Hg); 2) high concentrations of transition metals (>200 mg/L); 3) oxidizing agents (oxides of nitrogen) remaining following sample digestion.

Cold-Vapor AA uses a chemical reduction to reduce mercury selectively. The procedure is extremely sensitive but is subject to interferences from some volatile organics, chlorine, and sulfur compounds.

METHOD 6010

INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma atomic emission spectroscopy (ICP) determines elements including metals in solution. The method is applicable to a large number of metals and wastes. All matrices, including ground water, aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.

1.2 Elements for which Method 6010 is applicable are listed in Table 1. Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer. The data shown in Table 1 provide concentration ranges for clean aqueous samples. Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

1.3 The method of standard addition (MSA) (Paragraph 8.5.3) shall be used for the analysis of all EP extracts and sample digests unless either serial dilution or matrix spike addition demonstrates that it is not required.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods (e.g., Methods 3005-3050).

2.2 Method 6010 describes the simultaneous, or sequential, multielemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 3.0 should also be recognized and appropriate corrections made; tests for their presence are described in Section 8.5.

TABLE 1. RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Element	Wavelength[a] (nm)	Estimated Detection Limit[b] (ug/L)
Aluminum	308.215	45
Antimony	206.833	32
Arsenic	193.696	53
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	See note c
Selenium	196.026	75
Silicon	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

[a]The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Paragraph 3.1). In time, other elements may be added as more information becomes available and as required.

[b]The estimated instrumental detection limits shown are taken from Reference 1 in Section 10.0 below. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

[c]Highly dependent on operating conditions and plasma position.

3.0 INTERFERENCES

3.1 Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of simultaneous multielement instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed.

3.1.1 The interference is expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, argon flow rate, etc.

3.1.2 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferent concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

3.1.3 At present, information on the listed silver and potassium wavelengths is not available, but it has been reported that second-order energy from the magnesium 383.231-nm wavelength interferes with the listed potassium line at 766.491 nm.

3.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a

TABLE 2. ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM INTERFERENCE AT THE 100-mg/L LEVEL

Analyte	Wavelength (nm)	Interferent [a,b] Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Tl	V
Aluminum	308.215	—	—	—	—	—	—	0.21	—	—	1.4
Antimony	206.833	0.47	—	2.9	—	0.08	—	—	—	0.25	0.45
Arsenic	193.696	1.3	—	0.44	—	—	—	—	—	—	1.1
Barium	455.403	—	—	—	—	—	—	—	—	—	—
Beryllium	313.042	—	—	—	—	—	—	—	—	0.04	0.05
Boron	249.773	0.04	—	—	—	0.32	—	—	—	—	—
Cadmium	226.502	—	—	—	—	0.03	—	—	0.02	—	—
Calcium	317.933	—	—	0.08	—	0.01	0.01	0.04	—	0.03	0.03
Chromium	267.716	—	—	—	—	0.003	—	0.04	—	—	0.04
Cobalt	228.616	—	—	0.03	—	0.005	—	—	0.03	0.15	—
Copper	324.754	—	—	—	—	0.003	—	—	—	0.05	0.02
Iron	259.940	—	—	—	—	—	—	0.12	—	—	—
Lead	220.353	0.17	—	—	—	—	—	—	—	—	—
Magnesium	279.079	—	0.02	0.11	—	0.13	—	0.25	—	0.07	0.12
Manganese	257.610	0.005	—	0.01	—	0.002	0.002	—	—	—	—
Molybdenum	202.030	0.05	—	—	—	0.03	—	—	—	—	—
Nickel	231.604	—	—	—	—	—	—	—	—	—	—
Selenium	196.026	0.23	—	—	—	0.09	—	—	—	—	—
Silicon	288.158	—	—	0.07	—	—	—	—	—	—	0.01
Sodium	588.995	—	—	—	—	—	—	—	—	0.08	—
Thallium	190.864	0.30	—	—	—	—	—	—	—	—	—
Vanadium	292.402	—	—	0.05	—	0.005	—	—	—	0.02	—
Zinc	213.856	—	—	—	0.14	—	—	—	0.29	—	—

[a]Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

Al - 1000 mg/L,
Ca - 1000 mg/L,
Cr - 200 mg/L,
Cu - 200 mg/L
Fe - 1000 mg/L
Mg - 1000 mg/L,
Mn - 200 mg/L,
Tl - 200 mg/L,
V - 200 mg/L

[b]The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferent figure.

tip washer, or diluting the sample. Also, it has been reported that better control of the argon flow rate improves instrument performance; this is accomplished with the use of mass flow controllers.

3.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled argon plasma emission spectrometer:

4.1.1 **Computer-controlled emission spectrometer with background correction.**

4.1.2 **Radio frequency generator.**

4.1.3 **Argon gas supply:** Welding grade or better.

4.2 Operating conditions: The analyst should follow the instructions provided by the instrument's manufacturer. For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within instrument linear range where coordination factors are valid. The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

5.0 REAGENTS

5.1 Acids used in the preparation of standards and for sample processing must be reagent grade or better. Redistilled acids may be used.

5.1.1 **Concentrated hydrochloric acid (HCl).**

5.1.2 **Hydrochloric acid (1:1):** Add 500 mL concentrated HCl to 400 mL Type II water and dilute to 1 liter.

5.1.3 **Concentrated nitric acid (HNO_3).**

5.1.4 **Nitric acid (1:1):** Add 500 mL concentrated HNO_3 to 400 mL Type II water and dilute to 1 liter.

5.2 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.3 Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hr at 105°C, unless otherwise specified.

(CAUTION: **Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.**)

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure metal added, or with the use of the mole fraction and the weight of the metal salt added.

Metal

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

Metal salts

$$\text{Concentration (ppm)} = \frac{\text{weight (mg) x mole fraction}}{\text{volume (L)}}$$

5.3.1 **Aluminum solution**, stock, 1 mL = 100 ug Al: Dissolve 0.10 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4 mL of (1:1) HCl and 1 mL of concentrated HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of (1:1) HCl and dilute to 1,000 mL with Type II water.

5.3.2 **Antimony solution**, stock, 1 mL = 100 ug Sb: Dissolve 0.27 g $K(SbO)C_4H_4O_6$ (mole fraction Sb = 0.3749), weighed accurately to at least four significant figures, in Type II water, add 10 mL (1:1) HCl, and dilute to 1,000 mL with Type II water.

5.3.3 **Arsenic solution**, stock, 1 mL = 100 ug As: Dissolve 0.13 g of As_2O_3 (mole fraction As = 0.7574), weighed accurately to at least four significant figures, in 100 mL of Type II water containing 0.4 g NaOH. Acidify the solution with 2 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.4 **Barium solution**, stock, 1 mL = 100 ug Ba: Dissolve 0.15 g $BaCl_2$ (mole fraction Ba = 0.6595), dried at 250°C for 2 hr, weighed accurately to at least four significant figures, in 10 mL Type II water with 1 mL (1:1) HCl. Add 10.0 mL (1:1) HCl and dilute to 1,000 mL with Type II water.

5.3.5 **Beryllium solution**, stock, 1 mL = 100 ug Be: Do not dry. Dissolve 1.97 g $BeSO_4 \cdot 4H_2O$ (mole fraction Be = 0.0509), weighed accurately to at least four significant figures, in Type II water, add 10.0 ml concentrated HNO_3, and dilute to 1,000 mL with Type II water. Mole fraction = 0.0509.

5.3.6 **Boron solution**, stock 1 mL = 100 ug B: Do not dry. Dissolve 0.57 g anhydrous H_3BO_3 (mole fraction B = 0.1748), weighed accurately to at least four significant figures, in Type II water and dilute to 1,000 mL. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered, and store in a desiccator to prevent the entrance of atmospheric moisture.

5.3.7 **Cadmium solution**, stock, 1 mL = 100 ug Cd: Dissolve 0.11 g CdO (mole fraction Cd = 0.8754), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.8 **Calcium solution**, stock, 1 mL = 100 ug Ca: Suspend 0.25 g $CaCO_3$ (mole Ca fraction = 0.4005), dried at 180°C for 1 hr before weighing, weighed accurately to at least four significant figures, in Type II water and dissolve cautiously with a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.9 **Chromium solution**, stock, 1 mL = 100 ug Cr: Dissolve 0.19 g CrO_3 (mole fraction Cr = 0.5200), weighed accurately to at least four significant figures, in Type II water. When solution is complete, acidify with 10 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.10 **Cobalt solution**, stock, 1 mL = 100 ug Co: Dissolve 0.1000 g of cobalt metal, weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) HCl and dilute to 1,000 mL with Type II water.

5.3.11 **Copper solution**, stock, 1 mL = 100 ug Cu: Dissolve 0.13 g CuO (mole fraction Cu = 0.7989), weighed accurately to at least four significant figures), in a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.12 **Iron solution**, stock, 1 mL = 100 ug Fe: Dissolve 0.14 g Fe_2O_3 (mole fraction Fe = 0.6994), weighed accurately to at least four significant figures, in a warm mixture of 20 mL (1:1) HCl and 2 mL of concentrated HNO_3. Cool, add an additional 5.0 mL of concentrated HNO_3, and dilute to 1,000 mL with Type II water.

5.3.13 **Lead solution**, stock, 1 mL = 100 ug Pb: Dissolve 0.16 g $Pb(NO_3)_2$ (mole fraction Pb = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10 mL (1:1) HNO_3 and dilute to 1,000 mL with Type II water.

5.3.14 **Magnesium solution**, stock, 1 mL = 100 ug Mg: Dissolve 0.17 g MgO (mole fraction Mg = 0.6030), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.15 **Manganese solution**, stock, 1 mL = 100 ug Mn: Dissolve 0.1000 g of manganese metal, weighed accurately to at least four significant figures, in acid mixture (10 mL concentrated HCl and 1 mL concentrated HNO_3) and dilute to 1,000 mL with Type II water.

5.3.16 **Molybdenum solution**, stock, 1 mL = 100 ug Mo: Dissolve 0.20 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (mole fraction Mo = 0.5772), weighed accurately to at least four significant figures, in Type II water and dilute to 1,000 mL with Type II water.

5.3.17 **Nickel solution**, stock, 1 mL = 100 ug Ni: Dissolve 0.1000 g of nickel metal, weighed accurately to at least four significant figures, in 10.0 mL hot concentrated HNO_3, cool, and dilute to 1,000 mL with Type II water.

5.3.18 **Potassium solution**, stock, 1 mL = 100 ug K: Dissolve 0.19 g KCl (mole fraction K = 0.5244) dried at 110°C, weighed accurately to at least four significant figures, in Type II water and dilute to 1,000 mL.

5.3.19 **Selenium solution**, stock, 1 mL = 100 ug Se: Do not dry. Dissolve 0.17 g H_2SeO_3 (mole fraction Se = 0.6123), weighed accurately to at least four significant figures, in Type II water and dilute to 1,000 mL.

5.3.20 **Silica solution**, stock, 1 mL = 100 ug SiO_2: Do not dry. Dissolve 0.47 g $Na_2SiO_3\cdot 9H_2O$ (mole fraction Si = 0.09884), weighed accurately to at least four significant figures, in Type II water. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.21 **Silver solution**, stock, 1 mL = 100 ug Ag: Dissolve 0.16 g $AgNO_3$ (mole fraction Ag = 0.6350), weighed accurately to at least four significant figures, in Type II water and 10 mL concentrated HNO_3. Dilute to 1,000 mL with Type II water.

5.3.22 **Sodium solution**, stock, 1 mL = 100 ug Na: Dissolve 0.25 g NaCl (mole fraction Na = 0.3934), weighed accurately to at least four significant figures, in Type II water. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.23 **Thallium solution**, stock, 1 mL = 100 ug Tl: Dissolve 0.13 g $TlNO_3$ (mole fraction Tl = 0.7672), weighed accurately to at least four significant figures, in Type II water. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.24 **Vanadium solution**, stock, 1 mL = 100 ug V: Dissolve 0.23 g NH_4VO_3 (mole fraction V = 0.4356), weighed accurately to at least four significant figures, in a minimum amount of concentrated HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.25 **Zinc solution**, stock, 1 mL = 100 ug Zn: Dissolve 0.12 g ZnO (mole fraction Zn = 0.8034), weighed accurately to at least four significant figures, in a minimum amount of dilute HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.4 Mixed calibration standard solutions: Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Table 3). Add 2 mL (1:1) HNO_3 and 10 mL of (1:1) HCl and dilute to 100 mL with Type II water (see NOTE, below). Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see Paragraph 5.8) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should then be scanned using a sequential spectrometer to verify the absence of interelement spectral interference in the recommended mixed standard solutions.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of Type II water and warm the flask until the solution clears. Cool and dilute to 100 mL with Type II water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

TABLE 3. MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo, and Si
IV	Al, Ca, Cr, K, Na, and Ni
V	Ag (see Note to Paragraph 5.4), B, Mg, Sb, and Tl

5.5 Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

5.5.1 The **calibration blank** is prepared by diluting 2 mL of (1:1) HNO_3 and 10 mL of (1:1) HCl to 100 mL with Type II water. Prepare a sufficient quantity to flush the system between standards and samples.

5.5.2 The **reagent blank** must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

5.6 The instrument check standard is prepared by the analyst by combining compatible elements at concentrations equivalent to the midpoint of their respective calibration curves (see Paragraph 8.6.2.1 for use).

5.7 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the instrumental detection limits. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

5.8 The quality control sample should be prepared in the same acid matrix as the calibration standards at 10 times the instrumental detection limits and in accordance with the instructions provided by the supplier.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material in Chapter Three, Inorganic Analytes, Sections 3.1 through 3.3.

7.0 PROCEDURE

7.1 Preliminary treatment of all matrices is always necessary because of the complexity and variability of sample matrices. Solubilization and digestion procedures are presented in Sample Preparation Methods (Methods 3005-3050). The method of standard addition (MSA) (Paragraph 8.5.3) shall be used for the analysis of all EP extracts and sample digests unless either serial dilution or matrix spike addition demonstrates that it is not required. An internal standard may be substituted for the MSA.

7.2 Set up the instrument with proper operating parameters established in Paragraph 4.2. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration).

7.3 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Paragraph 5.4. Flush the system with the calibration blank (5.5.1) between each standard (see NOTE, below). (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.)

NOTE: For boron concentrations greater than 500 ug/L, extended flush times of 1 or 2 min may be required.

7.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

7.5 Flush the system with the calibration blank solution for at least 1 min (Paragraph 5.5.1) before the analysis of each sample (see Note to Paragraph 7.3). Analyze the instrument check standard (5.6) and the calibration blank (5.5.1) after each 10 samples.

7.6 Calculations: If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported in ug/L with up to three significant figures.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

8.3 Employ a minimum of one laboratory blank per sample batch to determine if contamination or any memory effects are occurring.

8.4 Analyze one duplicate sample for every 20 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

8.5 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 8.5.1 through 8.5.3, will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

8.5.1 **Serial dilution:** If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:4 dilution should agree within ±10% of the original determination. If not, a chemical or physical interference effect should be suspected.

8.5.2 **Matrix spike addition:** An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected. The use of a standard-addition analysis procedure can usually compensate for this effect.

CAUTION: The standard-addition technique does not detect coincident spectral overlap. If suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

8.5.3 **Standard addition:** The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of Volume V_X, are taken. To the first (labeled A) is added a small volume V_S of a standard analyte solution of concentration c_S. To the second (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration c_X is calculated:

$$c_X = \frac{S_B V_S c_S}{(S_A - S_B) V_X}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and c_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X, and thus c_S is much greater than c_X, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.

2. The chemical form of the analyte added must respond the same way as the analyte in the sample.

3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 1.

8.6 Check the instrument standardization by analyzing appropriate quality control check standards as follows.

8.6.1 Check instrument calibration using a calibration blank and two appropriate standards.

8.6.2 Verify calibration every 10 samples and at the end of the analytical run, using a calibration blank (5.5.1) and a single point check standard (5.6).

8.6.2.1 The results of the check standard are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

8.6.2.2 The results of the calibration blank are to agree within three standard deviations of the mean blank value. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples.

8.6.3 Verify the interelement and background correction factors at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Do this by analyzing the interference check sample (Paragraph 5.7). Results should be within $\pm$20% of the true value obtained in 8.6.2.1.

8.6.4 Duplicate spiked samples are to be analyzed at a frequency of 20%.

8.6.4.1 The relative percent difference between duplicate determinations is to be calculated as follows:

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100$$

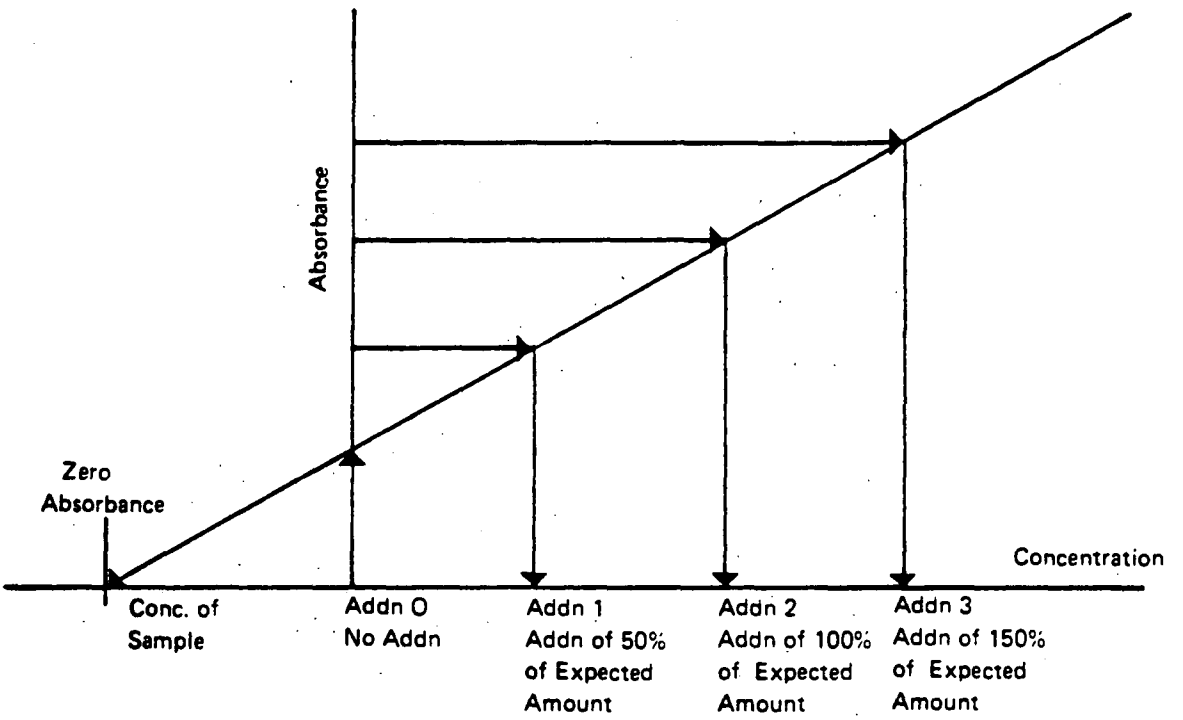


Figure 1. Standard Addition Plot.

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (duplicate).

(A control limit of ±20% for RPD shall be used for sample values greater than 10 times the instrument detection limit.)

8.6.4.2 The duplicate matrix spike sample recovery is to be within ±20% of the actual value.

8.6.5 The method of standard addition (Paragraph 8.5.3) shall be used for the analysis of all EP extracts.

9.0 METHOD PERFORMANCE

9.1 In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

9.2 In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was 9±2%. The mean percent recovery of spiked elements for all wastes was 93±6%. Spike levels ranged from 100 ug/L to 100 mg/L. The wastes included sludges and industrial wastewaters.

10.0 REFERENCES

1. Winge, R.K., V.J. Peterson, and V.A. Fassel, Inductively Coupled Plasma-Atomic Emission Spectroscopy: Prominent Lines, Final Report, March 1977 - February 1978, Ames Laboratory, Ames, IA, sponsored by Environmental Research Laboratory, Athens, GA, EPA-600/4-79-017, March 1979.

2. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-05, December 1982, Method 200.7.

3. Patel, B.K., Raab, G.A., et al., Report on a Single Laboratory Evaluation of Inductively Coupled Optical Emission Method 6010, EPA Contract No. 68-03-3050, December 1984.

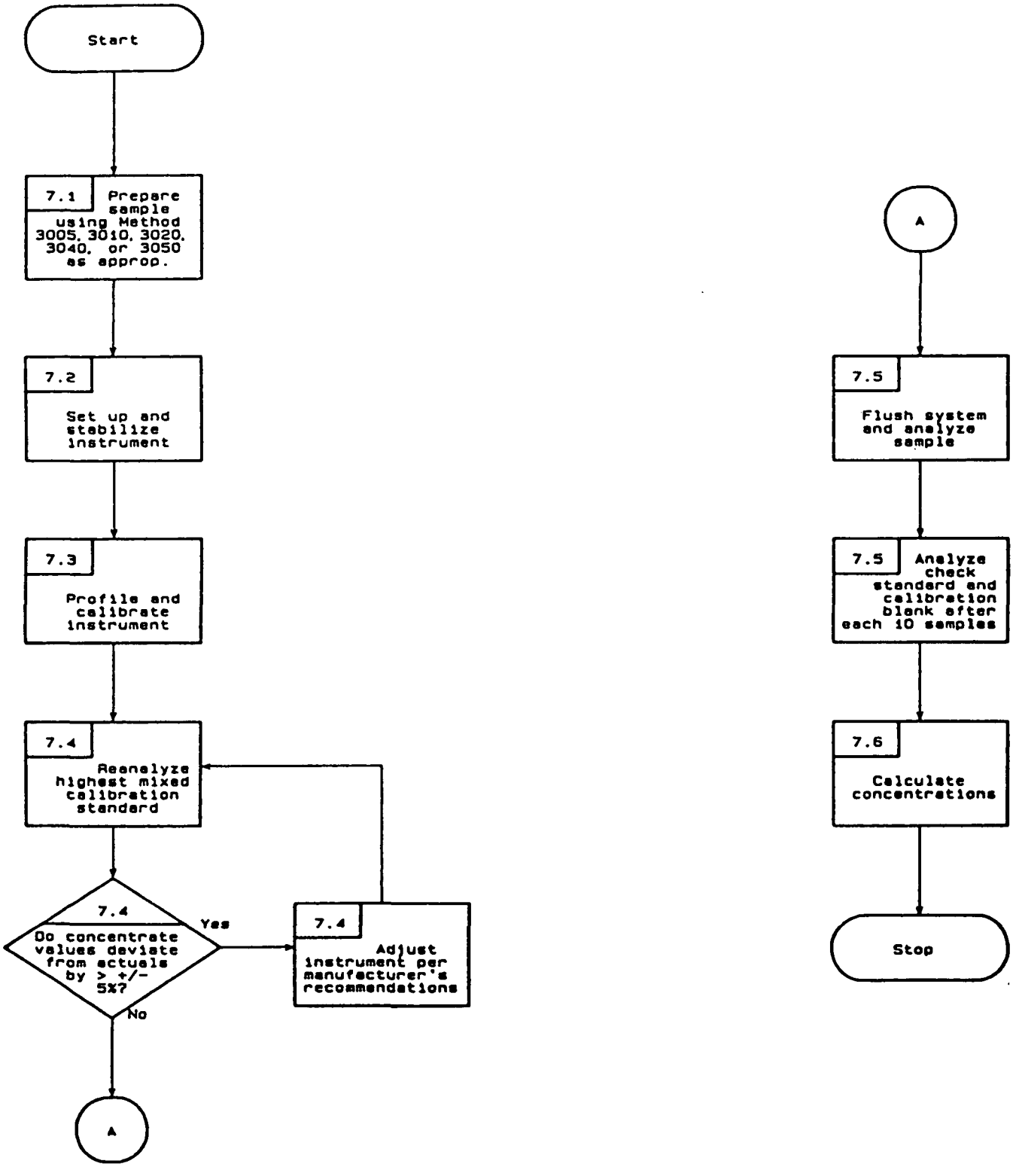
TABLE 4. ICP PRECISION AND ACCURACY DATA[a]

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True Value (ug/L)	Mean Reported Value (ug/L)	Mean SD[b] (%)	True Value (ug/L)	Mean Reported Value (ug/L)	Mean SD[b] (%)	True Value (ug/L)	Mean Reported Value (ug/L)	Mean SD[b] (%)
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	700	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se[c]	40	32	21.9	6	8.5	42	10	8.5	8.3

[a]Not all elements were analyzed by all laboratories.

[b]SD = standard deviation.

[c]Results for Se are from two laboratories.


Start
7.1 Prepare sample using Method 3005, 3010, 3020, 3040, or 3050 as approp.
7.2 Set up and stabilize instrument
7.3 Profile and calibrate instrument
7.4 Reanalyze highest mixed calibration standard
7.4 Do concentrate values deviate from actuals by > +/- 5%?
Yes
No
7.4 Adjust instrument per manufacturer's recommendations
A
A
7.5 Flush system and analyze sample
7.5 Analyze check standard and calibration blank after each 10 samples
7.6 Calculate concentrations
Stop

METHOD 7000

ATOMIC ABSORPTION METHODS

1.0 SCOPE AND APPLICATION

1.1 Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters and domestic and industrial wastes. While drinking water free of particulate matter may be analyzed directly, ground water, other aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion prior to analysis.

1.2 Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and models of atomic absorption spectrophotometers. The data shown in Table 1 provide some indication of the detection limits obtainable by direct aspiration and by furnace techniques. For clean aqueous samples, the detection limits shown in the table by direct aspiration may be extended downward with scale expansion and upward by using a less sensitive wavelength or by rotating the burner head. Detection limits by direct aspiration may also be extended through concentration of the sample and/or through solvent extraction techniques. For certain samples, lower concentrations may also be determined using the furnace techniques. The detection limits given in Table 1 are somewhat dependent on equipment (such as the type of spectrophotometer and furnace accessory, the energy source, the degree of electrical expansion of the output signal), and are greatly dependent on sample matrix. When using furnace techniques, however, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures which may result in either suppression or enhancement of the analysis element. To ensure valid data with furnace techniques, the analyst must examine each matrix for interference effects (see Paragraph 3.2.1) and, if detected, treat them accordingly, using either successive dilution, matrix modification, or method of standard additions (see Paragraph 8.7).

1.3 Where direct-aspiration atomic absorption techniques do not provide adequate sensitivity, reference is made to specialized procedures (in addition to the furnace procedure) such as the gaseous-hydride method for arsenic and selenium and the cold-vapor technique for mercury.

2.0 SUMMARY OF METHOD

2.1 Although methods have been reported for the analysis of solids by atomic absorption spectroscopy, the technique generally is limited to metals in solution or solubilized through some form of sample processing.

2.2 Preliminary treatment of waste water, ground water, EP extracts, and industrial waste is always necessary because of the complexity and

TABLE 1. ATOMIC ABSORPTION CONCENTRATION RANGES

Metal	Direct Aspiration		Furnace Procedure[a,c]
	Detection Limit (mg/L)	Sensitivity (mg/L)	Detection Limit (ug/L)
Aluminum	0.1	1	--
Antimony	0.2	0.5	3
Arsenic[b]	0.002	--	1
Barium(p)	0.1	0.4	--
Beryllium	0.005	0.025	0.2
Cadmium	0.005	0.025	0.1
Calcium	0.01	0.08	--
Chromium	0.05	0.25	1
Cobalt	0.05	0.2	1
Copper	0.02	0.1	--
Iron	0.03	0.12	--
Lead	0.1	0.5	1
Magnesium	0.001	0.007	--
Manganese	0.01	0.05	--
Mercury[d]	0.0002	--	--
Molybdenum(p)	0.1	0.4	1
Nickel(p)	0.04	0.15	--
Potassium	0.01	0.04	--
Selenium[b]	0.002	--	2
Silver	0.01	0.06	--
Sodium	0.002	0.015	--
Thallium	0.1	0.5	1
Tin	0.8	4	--
Vanadium(p)	0.2	0.8	4
Zinc	0.005	0.02	--

NOTE: The symbol (p) indicates the use of pyrolytic graphite with the furnace procedure.

[a]For furnace sensitivity values, consult instrument operating manual.

[b]Gaseous hydride method.

[c]The listed furnace values are those expected when using a 20-uL injection and normal gas flow, except in the cases of arsenic and selenium, where gas interrupt is used.

[d]Cold vapor technique.

variability of sample matrix. Solids, slurries, and suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. Solubilization and digestion procedures are presented in Section 3.2 (Sample Preparation Methods).

2.3 In direct-aspiration atomic absorption spectroscopy, a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp or an electrodeless discharge lamp is directed through the flame into a monochromator, and onto a detector that measures the amount of absorbed light. Absorption depends upon the presence of free unexcited ground-state atoms in the flame. Because the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

2.4 When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. As a greater percentage of available analyte atoms is vaporized and dissociated for absorption in the tube rather than the flame, the use of smaller sample volumes or detection of lower concentrations of elements is possible. The principle is essentially the same as with direct aspiration atomic absorption, except that a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground-state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground-state element in the vapor. The metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace, thereby causing the injected specimen to be volatilized. A monochromator isolates the characteristic radiation from the hollow cathode lamp or electrodeless discharge lamp, and a photosensitive device measures the attenuated transmitted radiation.

3.0 INTERFERENCES

3.1 Direct aspiration:

3.1.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or when the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome phosphate interference in magnesium, calcium, and barium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

3.1.2 Chemical interferences may also be eliminated by separating the metal from the interfering material. Although complexing agents are employed primarily to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

3.1.3 The presence of high dissolved solids in the sample may result in an interference from nonatomic absorbance such as light scattering. If background correction is not available, a nonabsorbing wavelength should be checked. Preferably, samples containing high solids should be extracted.

3.1.4 Ionization interferences occur when the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positively charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess (1,000 mg/L) of an easily ionized element such as K, Na, Li or Cs.

3.1.5 Spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Interference can also occur when resonant energy from another element in a multielement lamp, or from a metal impurity in the lamp cthode, falls within the bandpass of the slit setting when that other metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

3.1.6 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

3.1.7 All metals are not equally stable in the digestate, especially if it contains only HNO_3, not HNO_3 and HCl. The digestate should be analyzed as soon as possible, with preference given to Sn, Sb, Mo, Ba, and Ag.

3.2 Furnace procedure:

3.2.1 Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical interferences. The composition of the sample matrix can have a major effect on the analysis. It is those effects which must be determined and taken into consideration in the analysis of each different matrix encountered. To help verify the absence of matrix or chemical interference, the serial dilution technique (see Paragraph 8.6) may be used. Those samples which indicate the presence of interference should be treated in one or more of the following ways:

1. Successively dilute and reanalyze the samples to eliminate interferences.

2. Modify the sample matrix either to remove interferences or to stabilize the analyte. Examples are the addition of ammonium nitrate to remove alkali chlorides and the addition of ammonium phosphate to retain cadmium. The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.

3. Analyze the sample by method of standard additions while noticing the precautions and limitations of its use (see Paragraph 8.7.2).

3.2.2 Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, use either background correction or choose an alternate wavelength. Background correction may also compensate for nonspecific broad-band absorption interference.

3.2.3 Continuum background correction cannot correct for all types of background interference. When the background interference cannot be compensated for, chemically remove the analyte or use an alternate form of background correction, e.g., Zeeman background correction.

3.2.4 Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analyte.

3.2.5 Samples containing large amounts of organic materials should be oxidized by conventional acid digestion before being placed in the furnace. In this way, broad-band absorption will be minimized.

3.2.6 Anion interference studies in the graphite furnace indicate that, under conditions other than isothermal, the nitrate anion is preferred. Therefore, nitric acid is preferable for any digestion or solubilization step. If another acid in addition to HNO_3 is required, a minimum amount should be used. This applies particularly to hydrochloric and, to a lesser extent, to sulfuric and phosphoric acids.

3.2.7 Carbide formation resulting from the chemical environment of the furnace has been observed. Molybdenum may be cited as an example. When carbides form, the metal is released very slowly from the resulting metal carbide as atomization continues. Molybdenum may require 30 sec or more atomization time before the signal returns to baseline levels. Carbide formation is greatly reduced and the sensitivity increased with the use of pyrolytically coated graphite. Elements that readily form carbides are noted with the symbol (p) in Table 1.

3.2.8 For comments on spectral interference, see Paragraph 3.1.5.

3.2.9 Cross-contamination and contamination of the sample can be major sources of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed in Paragraph 4.8. Pipet tips are a frequent source of contamination. If suspected, they should be acid soaked with 1:5 HNO_3 and rinsed thoroughly with tap and deionized (Type II) water. The use of a better grade of pipet tip can greatly reduce this problem. Special attention should be given to reagent blanks in both analysis and in the correction of analytical results. Lastly, pyrolytic graphite, because of the production process and handling, can become contaminated. As many as five to ten high-temperature burns may be required to clean the tube before use.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer: Single- or dual-channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip-chart recorder.

4.2 Burner: The burner recommended by the particular instrument manufacturer should be used. For certain elements the nitrous oxide burner is required.

4.3 Hollow cathode lamps: Single-element lamps are preferred but multielement lamps may be used. Electrodeless discharge lamps may also be used when available.

4.4 Graphite furnace: Any furnace device capable of reaching the specified temperatures is satisfactory.

4.5 Strip-chart recorder: A recorder is recommended for furnace work so that there will be a permanent record and that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, peak shape, etc., can be easily recognized.

4.6 Pipets: Microliter, with disposable tips. Sizes can range from 5 to 100 uL as required. Pipet tips should be checked as a possible source of contamination prior to their use.

4.7 Pressure-reducing valves: The supplies of fuel and oxidant should be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

4.8 Glassware: All glassware, polypropylene, or Teflon containers, including sample bottles, should be washed in the following sequence: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap

water, and Type II water. (Chromic acid should not be used as a cleaning agent for glassware if chromium is to be included in the analytical scheme.) If it can be documented through an active analytical quality control program using spiked samples and reagent blanks that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

5.0 REAGENTS

5.1 Type II water (ASTM D1193): Use Type II water for the preparation of all reagents and calibration standards and as dilution water.

5.2 Concentrated nitric acid (HNO_3): Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with Type II water by adding the concentrated acid to an equal volume of water.

5.3 Hydrochloric acid (HCl, 1:1): Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with Type II water by adding the concentrated acid to an equal volume of water.

5.4 Fuel and oxidant: Commercial grade acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or a cylinder of compressed air. Reagent grade nitrous oxide is also required for certain determinations. Standard, commercially available argon and nitrogen are required for furnace work.

5.5 Stock standard metal solutions: Stock standard solutions are prepared from high purity metals, oxides, or nonhygroscopic reagent-grade salts using Type II water and redistilled nitric or hydrochloric acids. (See individual methods for specific instructions.) Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1,000 mg of the metal per liter. Commercially available standard solutions may also be used. Where the sample viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) may be used (see Paragraph 8.7).

5.6 Calibration standards: For those instruments which do not read out directly in concentration, a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards which produce an absorbance of 0.0 to 0.7. Calibration standards are prepared by diluting the stock metal solutions at the time of analysis. For best results, calibration standards should be prepared fresh each time a batch of samples is analyzed. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range of the linear part of the curve. The calibration standards should be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following processing. Beginning with the blank and working

toward the highest standard, aspirate the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure a reliable average reading for each solution. Calibration standards for furnace procedures should be prepared as described on the individual sheets for that metal.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material in Chapter Three, Metallic Analytes.

7.0 PROCEDURE

7.1 Preliminary treatment of waste water, ground water, EP extracts, and industrial waste is always necessary because of the complexity and variability of sample matrices. Solids, slurries, and suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. Solubilization and digestion procedures are presented in Chapter Three, Section 3.2, Sample Preparation Methods.

7.2 Direct aspiration (flame) procedure:

7.2.1 Differences between the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for a particular instrument. In general, after choosing the proper lamp for the analysis, allow the lamp to warm up for a minimum of 15 min, unless operated in a double-beam mode. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the current according to the manufacturer's recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant. Adjust the burner and nebulizer flow rate for maximum percent absorption and stability. Balance the photometer. Run a series of standards of the element under analysis. Construct a calibration curve by plotting the concentrations of the standards against absorbances. Set the curve corrector of a direct reading instrument to read out the proper concentration. Aspirate the samples and determine the concentrations either directly or from the calibration curve. Standards must be run each time a sample or series of samples is run.

7.3 Furnace procedure:

7.3.1 Furnace devices (flameless atomization) are a most useful means of extending detection limits. Because of differences between various makes and models of satisfactory instruments, no detailed operating instructions can be given for each instrument. Instead, the analyst should follow the instructions provided by the manufacturer of a particular instrument.

7.3.2 Background correction is important when using flameless atomization, especially below 350 nm. Certain samples, when atomized, may absorb or scatter light from the lamp. This can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high. Zeeman background correction is effective in overcoming composition or structured background interferences. It is particularly useful when analyzing for As in the presence of Al and when analyzing for Se in the presence of Fe.

7.3.3 Memory effects occur when the analyte is not totally volatilized during atomization. This condition depends on several factors: volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization, and furnace design. This situation is detected through blank burns. The tube should be cleaned by operating the furnace at full power for the required time period, as needed, at regular intervals during the series of determinations.

7.3.4 Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.3.5 To verify the absence of interference, follow the serial dilution procedure given in Paragraph 8.6.

7.3.6 A check standard should be run after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced. Tube life depends on sample matrix and atomization temperature. A conservative estimate would be that a tube will last at least 50 firings. A pyrolytic coating will extend that estimated life by a factor of three.

7.4 Calculation:

7.4.1 For determination of metal concentration by direct aspiration and furnace: Read the metal value in ug/L from the calibration curve or directly from the read-out system of the instrument.

7.4.2 If dilution of sample was required:

$$\text{ug/L metal in sample} = A \left(\frac{C + B}{C}\right)$$

where:

A = ug/L of metal in diluted aliquot from calibration curve.
B = Acid blank matrix used for dilution, mL.
C = sample aliquot, mL.

7.4.3 For solid samples, report all concentrations as ug/kg based on wet weight. Hence:

$$\text{ug metal/kg sample} = \frac{A \times V}{W}$$

where:

A = ug/L of metal in processed sample from calibration curve.
V = final volume of the processed sample, mL.
W = weight of sample, grams.

7.4.4 Different injection volumes must not be used for samples and standards. Instead, the sample should be diluted and the same size injection volume be used for both samples and standards. If dilution of the sample was required:

$$\text{ug/L of metal in sample} = Z \frac{(C + B)}{U}$$

where:

Z = ug/L of metal read from calibration curve or read-out system.
B = mL of acid blank matrix used for dilution.
C = mL of sample aliquot.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 A calibration curve must be prepared each day with a minimum of a reagent blank and three standards, verified by use of at least a reagent blank and one standard at or near the mid-range. Checks throughout the day must be within 20% of original curve.

8.3 If 20 or more samples per day are analyzed, the working standard curve must be verified by running an additional standard at or near the mid-range every 10 samples. Checks must be within $\pm$20% of true value.

8.4 At least one duplicate and one spike sample should be run every 20 samples, or with each matrix type to verify precision of the method.

8.5 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition may be used (see Section 8.7 below).

8.6 Serial dilution: Withdraw from the sample two equal aliquots. To one of the aliquots add a known amount of analyte and dilute both aliquots to the same predetermined volume. (The dilution volume should be based on the analysis of the undiluted sample. Preferably, the dilution should be 1:4, while keeping in mind that the diluted value should be at least 5 times the instrument detection limit. Under no circumstances should the dilution be less than 1:1.) The diluted aliquots should then be analyzed, and the unspiked results, multiplied by the dilution factor, should be compared to the original determination. Agreement of the results (within 10%) indicates the absence of interference. Comparison of the actual signal from the spike with the expected response from the analyte in an aqueous standard should help confirm the finding from the dilution analysis.

8.7 Method of standard additions:

8.7.1 In the simplest version of this method, equal volumes of sample are added to a deionized distilled (Type II) water blank and to a standard (refer to Paragraph 8.7.3). If a higher degree of accuracy is required, more than one addition should be made. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 1.

8.7.2 The method of standard additions can be very useful; however, for the results to be valid the following limitations must be taken into consideration:

a. The absorbance plot of sample and standards must be linear over the concentration range of concern. For best results, the slope of the plot should be nearly the same as the slope of the aqueous standard curve. If the slope is significantly different (more than 20%), caution should be exercised.

b. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

c. The determination must be free of spectral interference and corrected for nonspecific background interference.

8.7.3 The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of Volume V_X, are taken. To the first (labeled A) is added a small volume V_S of a standard analyte solution of concentration c_S. To the second (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration c_X is calculated:

$$c_X = \frac{S_B V_S c_S}{(S_A - S_B) V_X}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and c_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X, and thus c_S is much greater than c_X, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

9.0 METHOD PERFORMANCE

9.1 See individual methods.

10.0 REFERENCES

1. U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020 (revised March 1983).

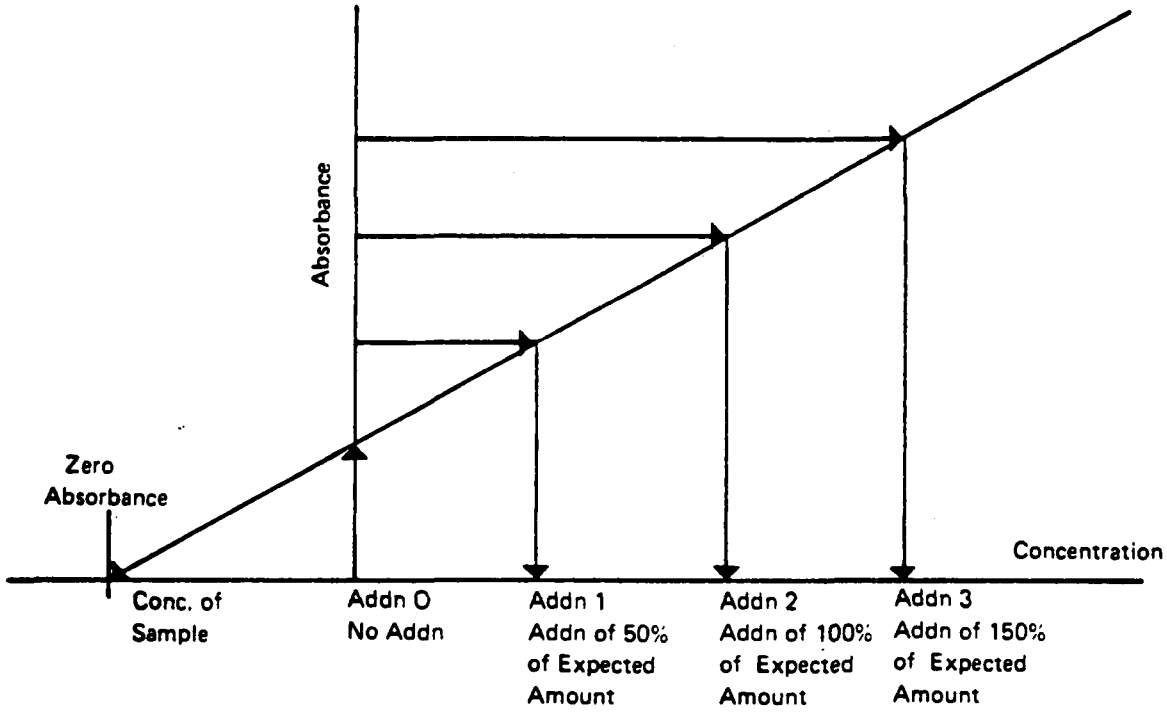
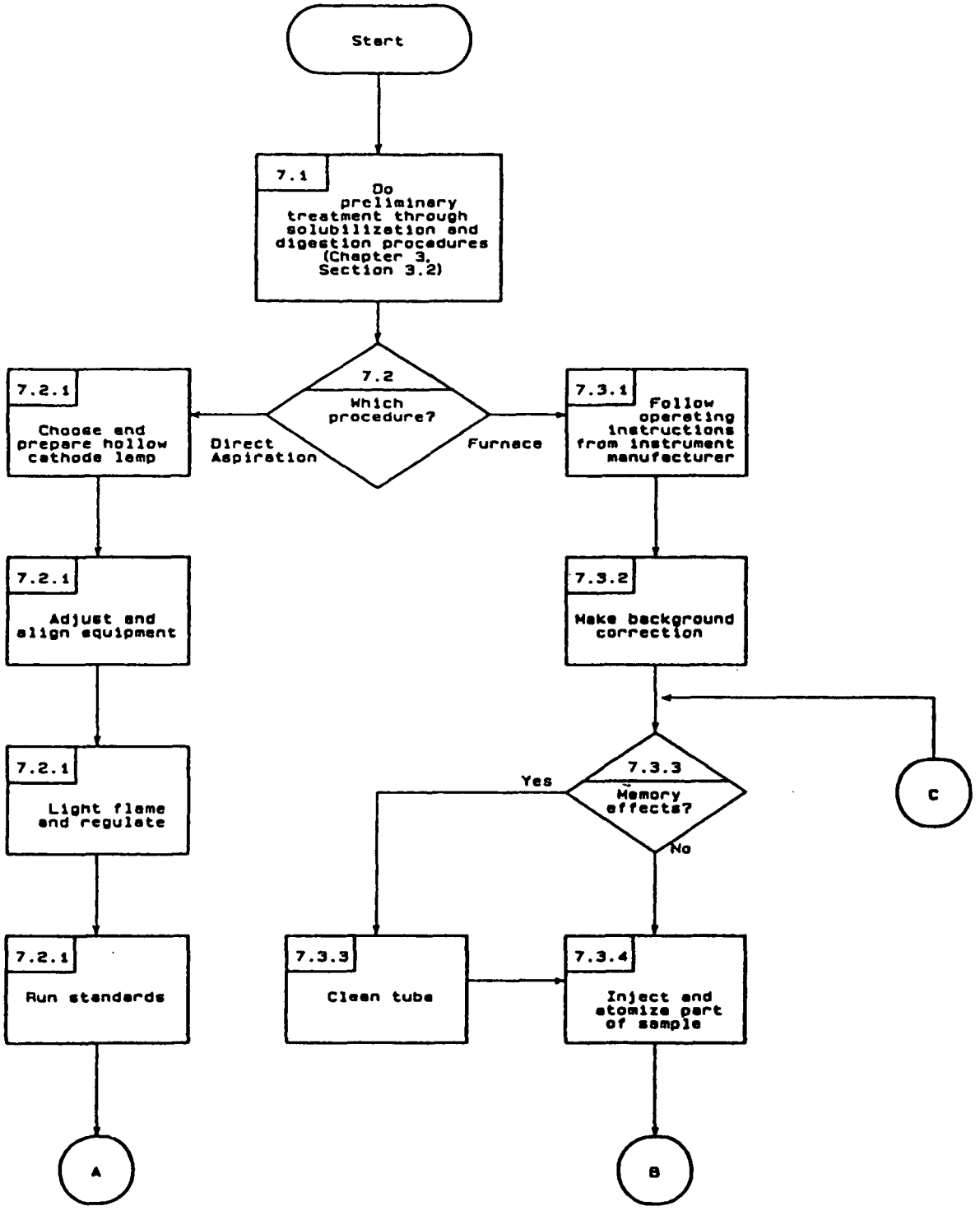
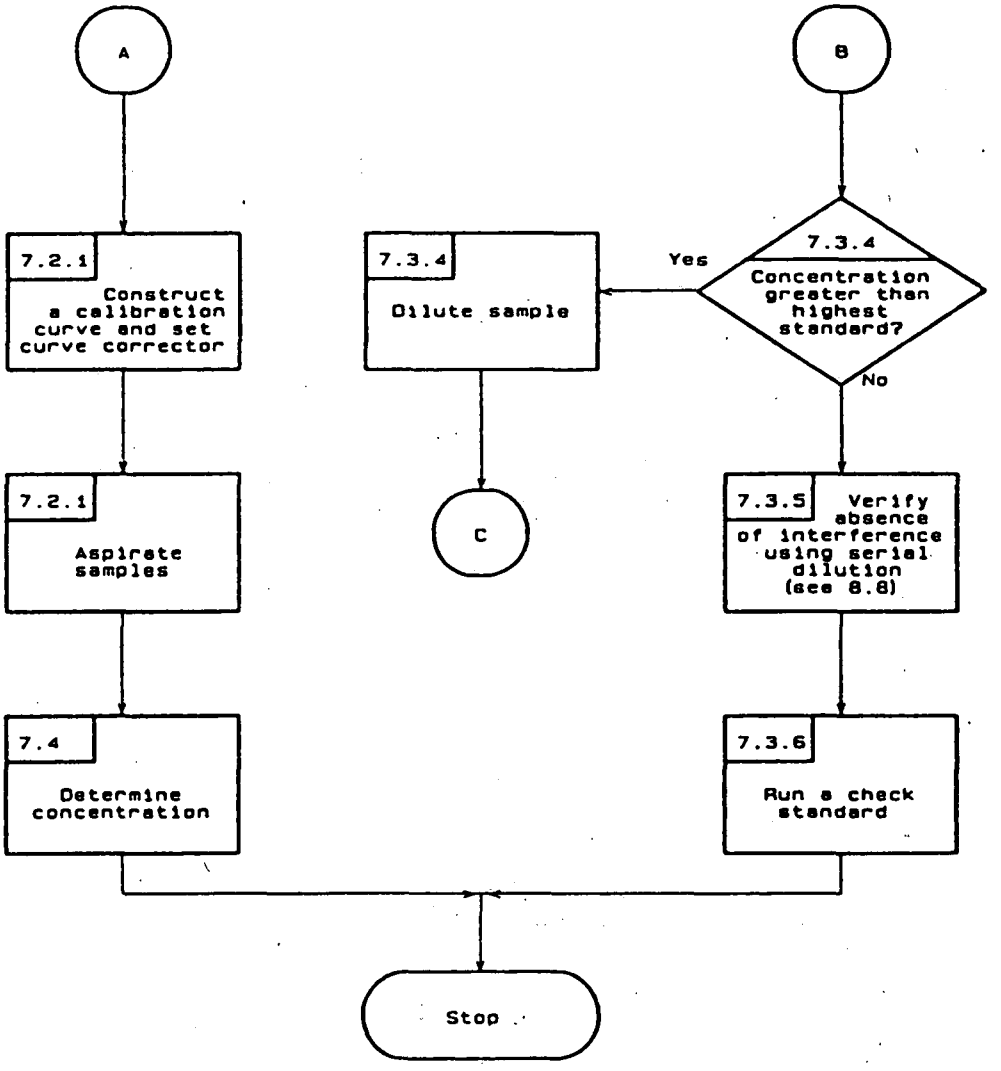


Figure 1. Standard Addition Plot.


Start
7.1
Do preliminary treatment through solubilization and digestion procedures (Chapter 3, Section 3.2)
7.2
Which procedure?
Direct Aspiration
Furnace
7.2.1
Choose and prepare hollow cathode lamp
7.2.1
Adjust and align equipment
7.2.1
Light flame and regulate
7.2.1
Run standards
A
7.3.1
Follow operating instructions from instrument manufacturer
7.3.2
Make background correction
7.3.3
Memory effects?
Yes
No
C
7.3.3
Clean tube
7.3.4
Inject and atomize part of sample
B


A
B
7.2.1
Construct a calibration curve and set curve corrector
7.3.4
Dilute sample
Yes
7.3.4
Concentration greater than highest standard?
No
7.2.1
Aspirate samples
C
7.3.5
Verify absence of interference using serial dilution (see 8.8)
7.4
Determine concentration
7.3.6
Run a check standard
Stop

METHOD 7020

ALUMINUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Aluminum may be as much as 15% ionized in a nitrous-oxide/acetylene flame. Use of an ionization suppressor (1,000 ug/mL K as KCl) as in Method 7000, Paragraph 3.1.4, will eliminate this interference.

3.3 Aluminum is a very common contaminant, and great care should be taken to avoid contamination.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Aluminum hollow cathode lamp.**
4.2.2 **Wavelength:** 324.7 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Nitrous oxide.
4.2.5 **Type of flame:** Fuel rich.
4.2.6 **Background correction:** Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g of aluminum metal in dilute HCl with gentle warming. Dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

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5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing. Samples and standards should also contain 2 mL KCl/100 mL solution (Paragraph 3.2 above).

5.3 Potassium chloride solution: Dissolve 95 g potassium chloride (KCl) in Type II water and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

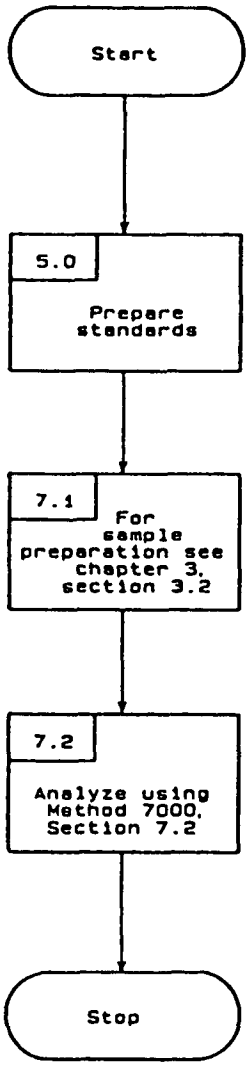
9.1 Precision and accuracy data are available in Method 202.1 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 5-50 mg/L, with a wavelength of 309.3 nm.
Sensitivity: 1 mg/L.
Detection limit: 0.1 mg/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, Method 202.1, December 1982.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7040

ANTIMONY (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 In the presence of lead (1,000 mg/L), a spectral interference may occur at the 217.6-nm resonance line. In this case, the 231.1-nm antimony line should be used.

3.3 Increasing the acid concentrations decreases the antimony absorption. To avoid this effect, the acid concentration in the samples and in the standards should be matched.

3.4 Excess concentrations of copper and nickel (and possibly other elements), as well as acids, can interfere with antimony analyses. If the sample contains these matrix types, either matrices of the standards should be matched to those of the sample or the sample should be analyzed using a nitrous oxide/acetylene flame.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Antimony hollow cathode lamp or electrodeless discharge lamp.**
4.2.2 **Wavelength:** 217.6 nm (primary); 231.1 nm (secondary).
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Fuel lean.
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

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5.2 Preparation of standards:

5.2.1 **Stock solution:** Carefully weigh 2.7426 g of antimony potassium tartrate, $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$ (analytical reagent grade), and dissolve in Type II water. Dilute to 1 liter with Type II water; 1 mL = 1 mg Sb (1,000 mg/L). Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should contain 0.2% (v/v) HNO_3 and 1-2% v/v HCl, prepared using the same types of acid and at the same concentrations as in the sample after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Method 3005. Method 3005, a soft digestion, is presently the only digestion procedure recommended for Sb. It yields better recoveries than either Method 3010 or Method 3050. There is no hard digestion for Sb at this time.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration Procedure.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

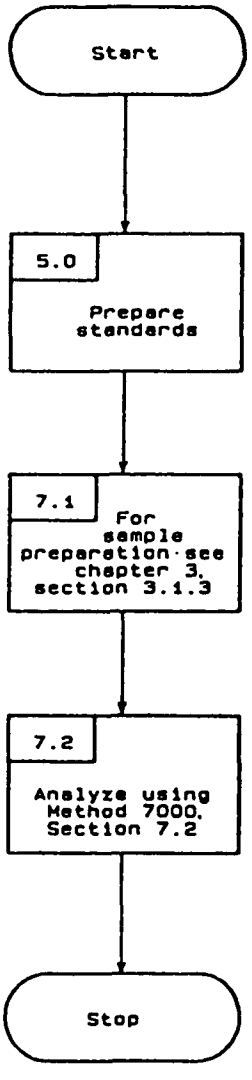
Optimum concentration range: 1-40 mg/L with a wavelength of 217.6 nm.
Sensitivity: 0.5 mg/L.
Detection limit: 0.2 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 5.0 and 15 mg Sb/L gave the standard deviations of $\pm$0.08 and $\pm$0.1, respectively. Recoveries at these levels were 96% and 97%, respectively.

9.3 For concentrations of antimony below 0.35 mg/L, the furnace procedure (Method 7041) is recommended.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 204.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.1.3
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7041

ANTIMONY (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 High lead concentration may cause a measurable spectral interference on the 217.6-nm line. If this interference is expected, the secondary wavelength should be employed or Zeeman background correction used.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Drying time and temp:** 30 sec at 125°C.
4.2.2 **Ashing time and temp:** 30 sec at 800°C.
4.2.3 **Atomizing time and temp:** 10 sec at 2700°C.
4.2.4 **Purge gas:** Argon or nitrogen.
4.2.5 **Wavelength:** 217.6 nm (primary); 231.1 nm (alternate).
4.2.6 **Background correction:** Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Carefully weigh 2.7426 g of antimony potassium tartrate (analytical reagent grade) and dissolve in Type II water. Dilute to 1 liter with Type II water; 1 mL = 1 mg Sb (1,000 mg/L). Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should contain 0.2% (v/v) HNO_3 and 1-2% (v/v) HCl, prepared using the same types of acid and at the same concentrations as in the sample after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Method 3005. Method 3005, a soft digestion, is presently the only digestion procedure recommended for Sb. It yields better recoveries than either Method 3010 or Method 3050. There is no hard digestion for Sb at this time.

NOTE: The addition of HCl acid to the digestate prevents the furnace analysis of this digestate for many other metals.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

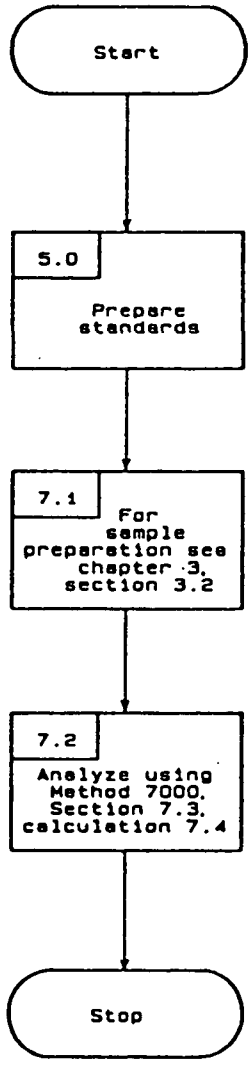
9.1 Precision and accuracy data are not available at this time.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 20-300 ug/L.
Detection limit: 3 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 204.2.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.3, calculation 7.4
Stop

METHOD 7060

ARSENIC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7060 is an atomic absorption procedure approved for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7060, samples must be prepared in order to convert organic forms of arsenic to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050.

2.2 Following the appropriate dissolution of the sample, a representative aliquot of the digestate is spiked with a nickel nitrate solution and is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode or EDL radiation during atomization will be proportional to the arsenic concentration.

2.3 The typical detection limit for this method is 1 ug/L.

3.0 INTERFERENCES

3.1 Elemental arsenic and many of its compounds are volatile; therefore, samples may be subject to losses of arsenic during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A nickel nitrate solution must be added to all digestates prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, arsenic analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Arsenic analysis is particularly susceptible to these problems because of its low analytical wavelength (193.7 nm). Simultaneous background

correction must be employed to avoid erroneously high results. Aluminum is a severe positive interferent in the analysis of arsenic, especially using D_2 arc background correction. Zeeman background correction is very useful in this situation.

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected by means of blank burns, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beaker: 250 mL.

4.2 Volumetric flasks: 10-mL.

4.3 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip-chart recorder.

4.4 Arsenic hollow cathode lamp, or electrodeless discharge lamp (EDL): EDLs provide better sensitivity for arsenic analysis.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Strip-chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1,000 uL, as required.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If a method blank using the acid is <MDL, the acid can be used.

5.3. Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If a method blank using the H_2O_2 is <MDL, the acid can be used.

5.4 Arsenic standard stock solution (1,000 mg/L): Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide (As_2O_3, analytical reagent grade) or equivalent in 100 mL of Type II water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter (1 mL = 1 mg As).

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ or equivalent in Type II water and dilute to 100 mL.

5.6 Nickel nitrate solution (1%): Dilute 20 mL of the 5% nickel nitrate to 100 mL with Type II water.

5.7 Arsenic working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add 1 mL of concentrated HNO_3, 2 mL of 30% H_2O_2, and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with Type II water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Paragraphs 7.1.1-7.1.3. Sludge-type samples should be prepared according to Method 3050. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer 100 mL of well-mixed sample to a 250-mL Griffin beaker; add 2 mL of 30% H_2O_2 and sufficient concentrated HNO_3 to result in an acid concentration of 1% (v/v). Heat for 1 hr at 95°C or until the volume is slightly less than 50 mL.

7.1.2 Cool and bring back to 50 mL with Type II water.

7.1.3 Pipet 5 mL of this digested solution into a 10-mL volumetric flask, add 1 mL of the 1% nickel nitrate solution, and dilute to 10 mL with Type II water. The sample is now ready for injection into the furnace.

7.2 The 193.7-nm wavelength line and a background correction system are required. Follow the manufacturer's suggestions for all other spectrophotometer parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.5 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions.

7.6 Run a check standard after every 10 injections of samples. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.7 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased samples must be appropriately qualified (e.g., 5 ug/g aqueous phase).

7.8 Duplicates, spiked samples, and check standards should be routinely analyzed.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 20 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 206.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The optimal concentration range for this method is 5-100 ug/L.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

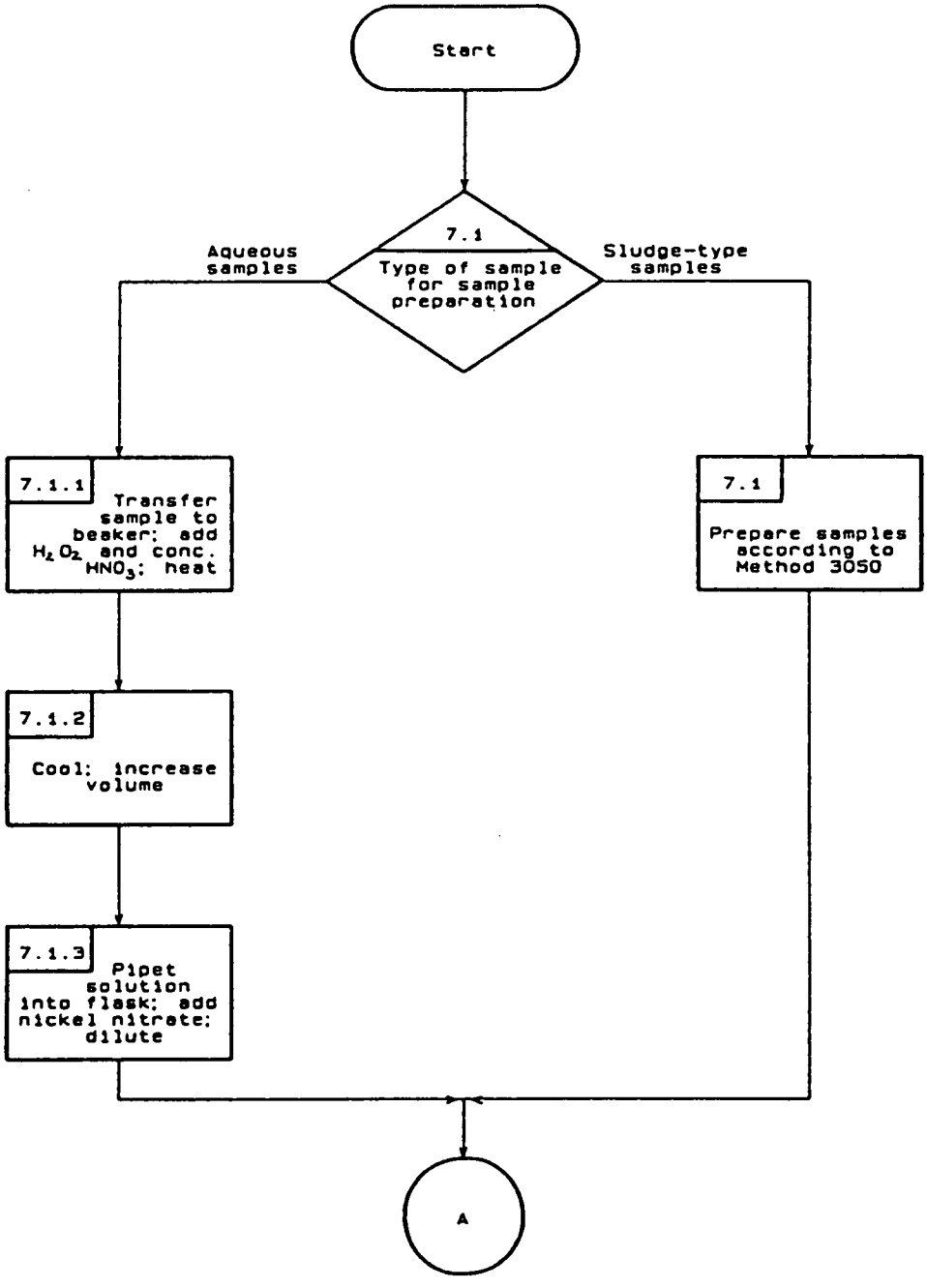
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.2.

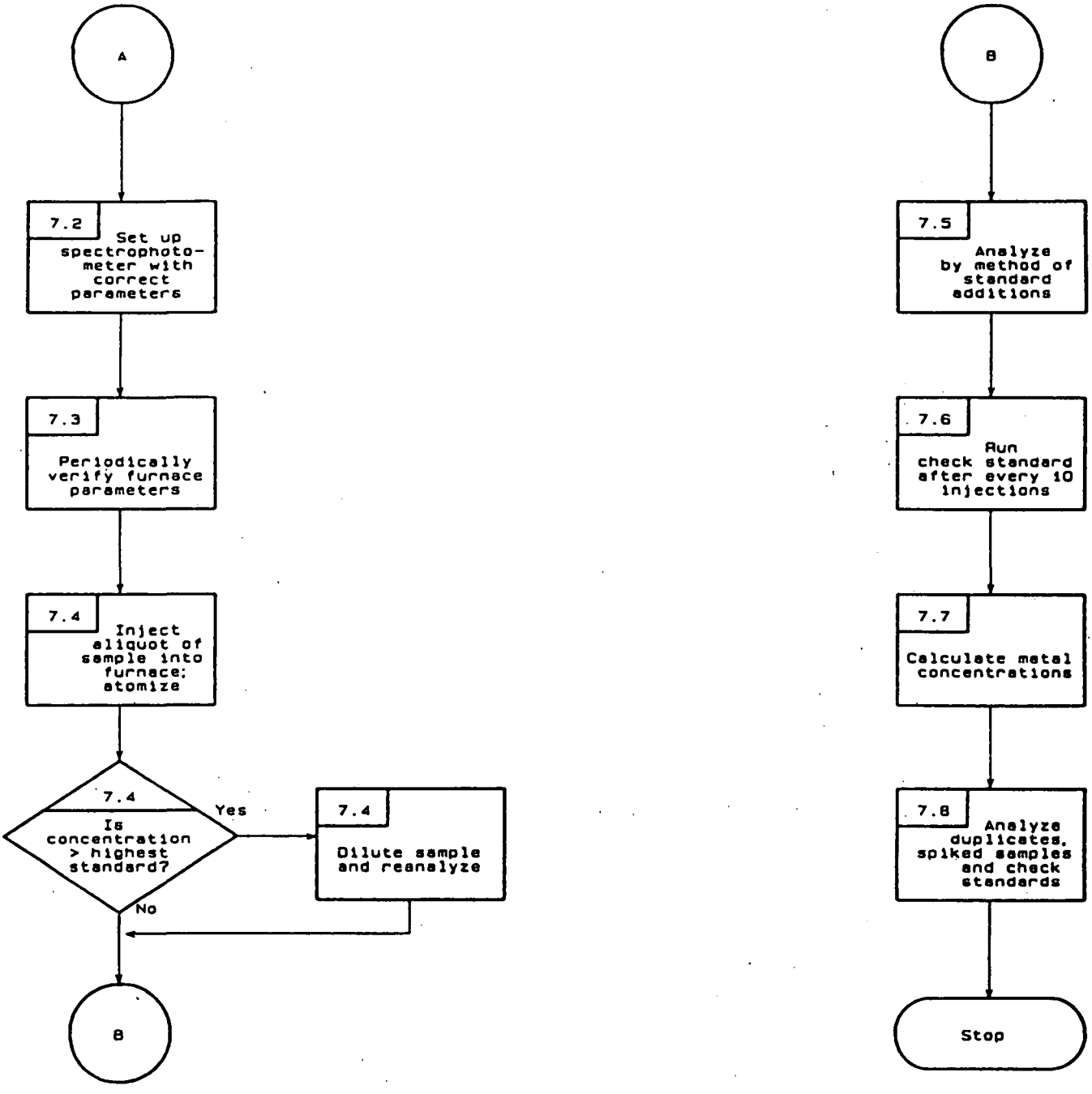
2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Contaminated soil	3050	2.0, 1.8 ug/g
Oily soil	3050	3.3, 3.8 ug/g
NBS SRM 1646 Estuarine sediment	3050	8.1, 8.33 ug/g[a]
Emission control dust	3050	430, 350 ug/g

[a]Bias of -30 and -28% from expected, respectively.


Start
7.1
Type of sample for sample preparation
Aqueous samples
Sludge-type samples
7.1.1
Transfer sample to beaker; add H_2O_2 and conc. HNO_3; heat
7.1.2
Cool; increase volume
7.1.3
Pipet solution into flask; add nickel nitrate; dilute
7.1
Prepare samples according to Method 3050
A


A
7.2
Set up spectrophotometer with correct parameters
7.3
Periodically verify furnace parameters
7.4
Inject aliquot of sample into furnace; atomize
7.4
Is concentration > highest standard?
Yes
No
7.4
Dilute sample and reanalyze
B
B
7.5
Analyze by method of standard additions
7.6
Run check standard after every 10 injections
7.7
Calculate metal concentrations
7.8
Analyze duplicates, spiked samples and check standards
Stop

METHOD 7061

ARSENIC (ATOMIC ABSORPTION, GASEOUS HYDRIDE)

1.0 SCOPE AND APPLICATION

1.1 Method 7061 is an atomic absorption procedure for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and ground water. Method 7061 is approved only for sample matrices that do not contain high concentrations of chromium, copper, mercury, nickel, silver, cobalt, and molybdenum. All samples must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are employed to determine the applicability of the method to a given waste.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric/sulfuric acid digestion procedure described in this method (Paragraph 7.1). Next, the arsenic in the digestate is reduced to the trivalent form with tin chloride. The trivalent arsenic is then converted to a volatile hydride using hydrogen produced from a zinc/HCl reaction.

2.2 The volatile hydride is swept into an argon-hydrogen flame located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the lamp radiation is proportional to the arsenic concentration.

2.3 The typical detection limit for this method is 0.002 mg/L.

3.0 INTERFERENCES

3.1 High concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver can cause analytical interferences.

3.2 Traces of nitric acid left following the sample work-up can result in analytical interferences. Nitric acid must be distilled off by heating the sample until fumes of SO_3 are observed.

3.3 Elemental arsenic and many of its compounds are volatile; therefore, certain samples may be subject to losses of arsenic during sample preparation.

4.0 APPARATUS AND MATERIALS

4.1 Beaker: 100-mL.

4.2 Electric hot plate.

4.3 A commercially available zinc slurry/hydride generator or a generator constructed from the following materials (see Figure 1):

4.3.1 **Medicine dropper:** Capable of fitting into a size "0" rubber stopper and delivering 1.5 mL.

4.3.2 **Pear-shaped reaction flask:** 50-mL, with two 14/20 necks (Scientific Glass JM-5835).

4.3.3 **Gas inlet-outlet tube:** Constructed from a micro cold-finger condenser (JM-3325) by cutting the portion below the 14/20 ground-glass joint.

4.3.4 **Magnetic stirrer:** To homogenize the zinc slurry.

4.3.5 **Polyethylene drying tube:** 10-cm, filled with glass to prevent particulate matter from entering the burner.

4.3.6 **Flow meter:** Capable of measuring 1 liter/min.

4.4 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip-chart recorder.

4.5 Burner: Recommended by the particular instrument manufacturer for the argon-hydrogen flame.

4.6 Arsenic hollow cathode lamp or arsenic electrodeless discharge lamp.

4.7 Strip-chart recorder.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid (HNO_3): Acid should be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.3 Concentrated sulfuric acid (H_2SO_4): Acid should be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.4 Concentrated hydrochloric acid (HCl): Acid should be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

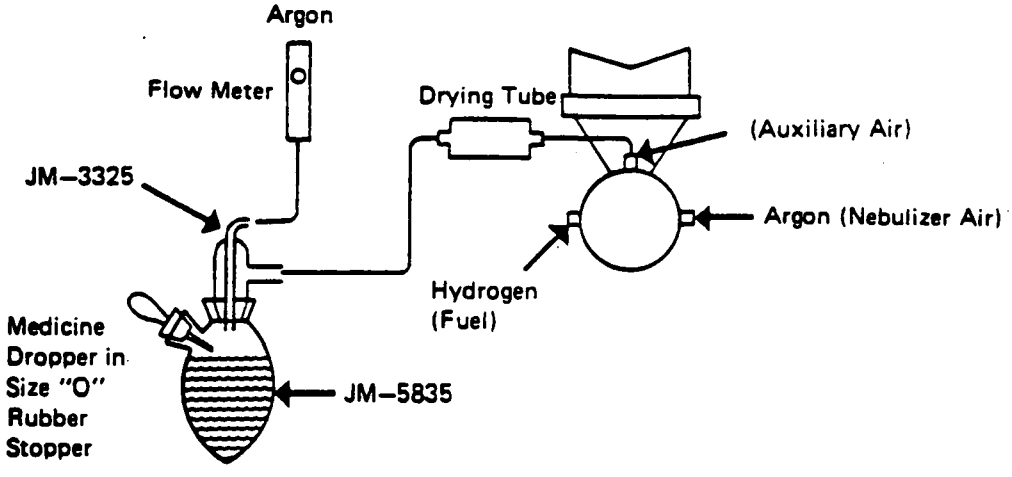


Figure 1. Zinc slurry hydride generator apparatus set-up and AAS sample introduction system.

5.5 Diluent: Add 100 mL 18 N H_2SO_4 and 400 mL concentrated HCl to 400 mL Type II water and dilute to a final volume of 1 liter with Type II water.

5.6 Potassium iodide solution: Dissolve 20 g KI in 100 mL Type II water.

5.7 Stannous chloride solution: Dissolve 100 g $SnCl_2$ in 100 mL concentrated HCl.

5.8 Arsenic solutions:

5.8.1 **Arsenic standard solution** (1,000 mg/L): Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide As_2O_3 (analytical reagent grade) or equivalent in 100 mL of Type II water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter.

5.8.2 **Intermediate arsenic solution:** Pipet 1 mL stock arsenic solution into a 100-mL volumetric flask and bring to volume with Type II water containing 1.5 mL concentrated HNO_3/liter (1 mL = 10 ug As).

5.8.3 **Standard arsenic solution:** Pipet 10 mL intermediate arsenic solution into a 100-mL volumetric flask and bring to volume with Type II water containing 1.5 mL concentrated HNO_3/liter (1 mL = 1 ug As).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Place a 50-mL aliquot of digested sample (or, in the case of analysis of EP extracts, 50 mL) of the material to be analyzed in a 100-mL beaker. Add 10 mL concentrated HNO_3 and 12 mL 18 N H_2SO_4. Evaporate the

sample in the hood on an electric hot plate until white SO_3 fumes are observed (a volume of about 20 mL). Do not let the sample char. If charring occurs, immediately turn off the heat, cool, and add an additional 3 mL of HNO_3. Continue to add additional HNO_3 in order to maintain an excess (as evidenced by the formation of brown fumes). Do not let the solution darken, because arsenic may be reduced and lost. When the sample remains colorless or straw yellow during evolution of SO_3 fumes, the digestion is complete. Cool the sample, add about 25 mL Type II water, and again evaporate until SO_3 fumes are produced in order to expel oxides of nitrogen. Cool. Transfer the digested sample to a 100-mL volumetric flask. Add 40 mL of concentrated HCl and bring to volume with Type II water.

7.2 Prepare working standards from the standard arsenic solution. Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of standard to 100-mL volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20, and 25 ug As/liter.

7.3 If EP extracts are being analyzed or if a matrix interference is encountered, take the 15-, 20-, and 25-mg/liter standards and quantitatively transfer 25 mL of each of these standards into separate 50-mL volumetric flasks. Add 10 mL of the prepared sample to each flask. Bring to volume with Type II water containing 1.5 mL HCl/liter.

7.4 Add 10 mL of prepared sample to a 50-mL volumetric flask. Bring to volume with Type II water containing 1.5 mL HCl/liter. This is the zero addition aliquot.

NOTE: The absorbance from the zero addition aliquot will be one-fifth that produced by the prepared sample. The absorbance from the spiked samples will be one-half that produced by the standards plus the contribution from one-fifth of the prepared sample. Keeping these absorbances in mind will assist in judging the correct dilutions to produce optimum absorbance.

7.5 Transfer a 25-mL portion of the digested sample or standard to the reaction vessel and add 1 mL KI solution. Add 0.5 mL $SnCl_2$ solution. Allow at least 10 min for the metal to be reduced to its lowest oxidation state. Attach the reaction vessel to the special gas inlet-outlet glassware. Fill the medicine dropper with 1.50 mL zinc slurry that has been kept in suspension with the magnetic stirrer. Firmly insert the stopper containing the medicine dropper into the side neck of the reaction vessel. Squeeze the bulb to introduce the zinc slurry into the sample or standard solution. The metal hydride will produce a peak almost immediately. After the recorder pen begins to return to the base line, the reaction vessel can be removed.

CAUTION: Arsine is very toxic. Precautions must be taken to avoid inhaling arsine gas.

7.6 Use the 193.7-nm wavelength and background correction for the analysis of arsenic.

7.7 Follow the manufacturer's instructions for operating an argon-hydrogen flame. The argon-hydrogen flame is colorless; therefore, it may be useful to aspirate a low concentration of sodium to ensure that ignition has occurred.

7.8 If the method of standard additions was employed, plot the absorbances of spiked samples and blank vs. the concentrations. The extrapolated value will be one-fifth the concentration of the original sample. If the plot does not result in a straight line, a nonlinear interference is present. This problem can sometimes be overcome by dilution or addition of other reagents if there is some knowledge about the waste. If the method of standard additions was not required, then the concentration can be part of the calibration curve.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 20 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

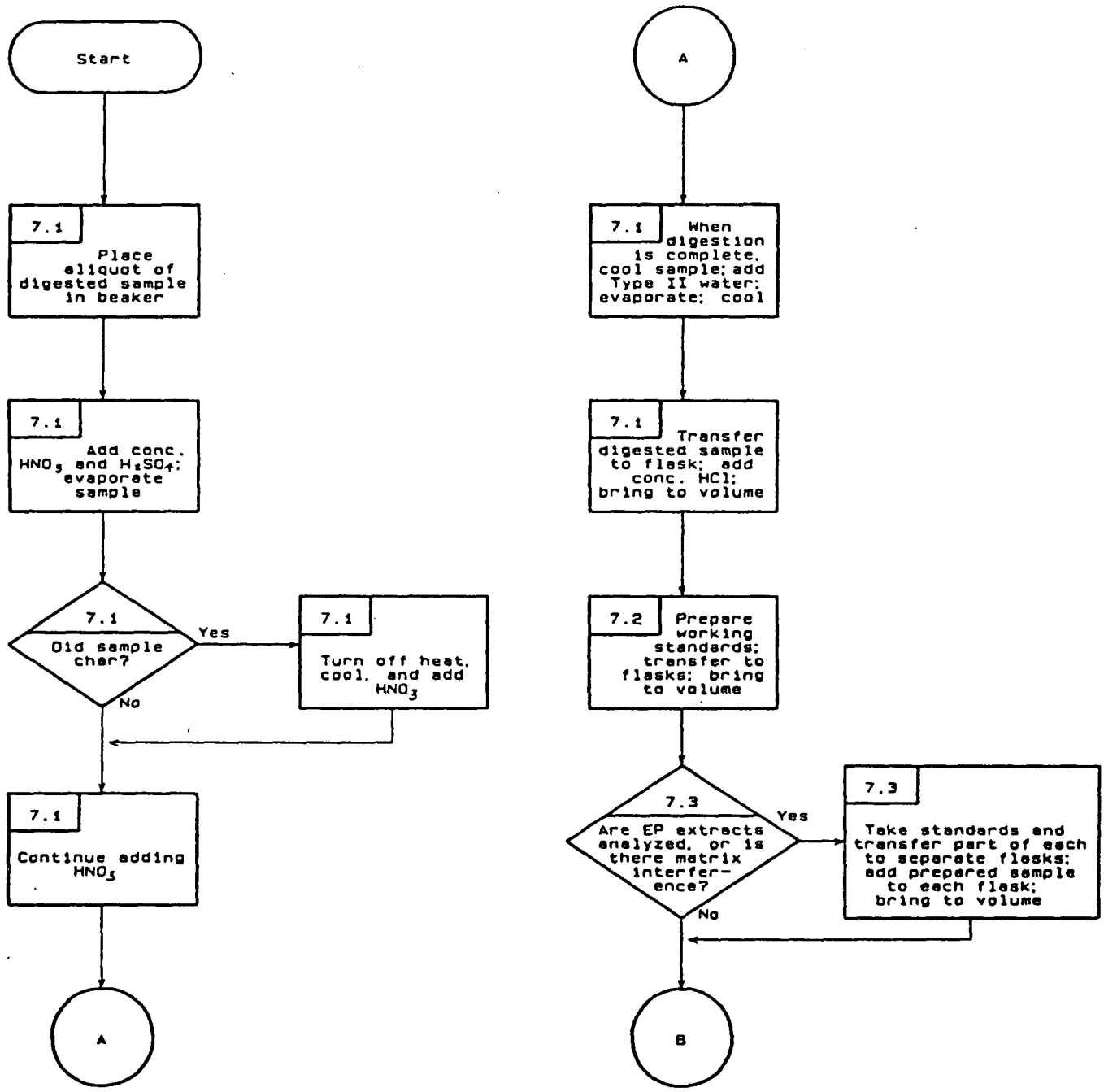
8.7 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

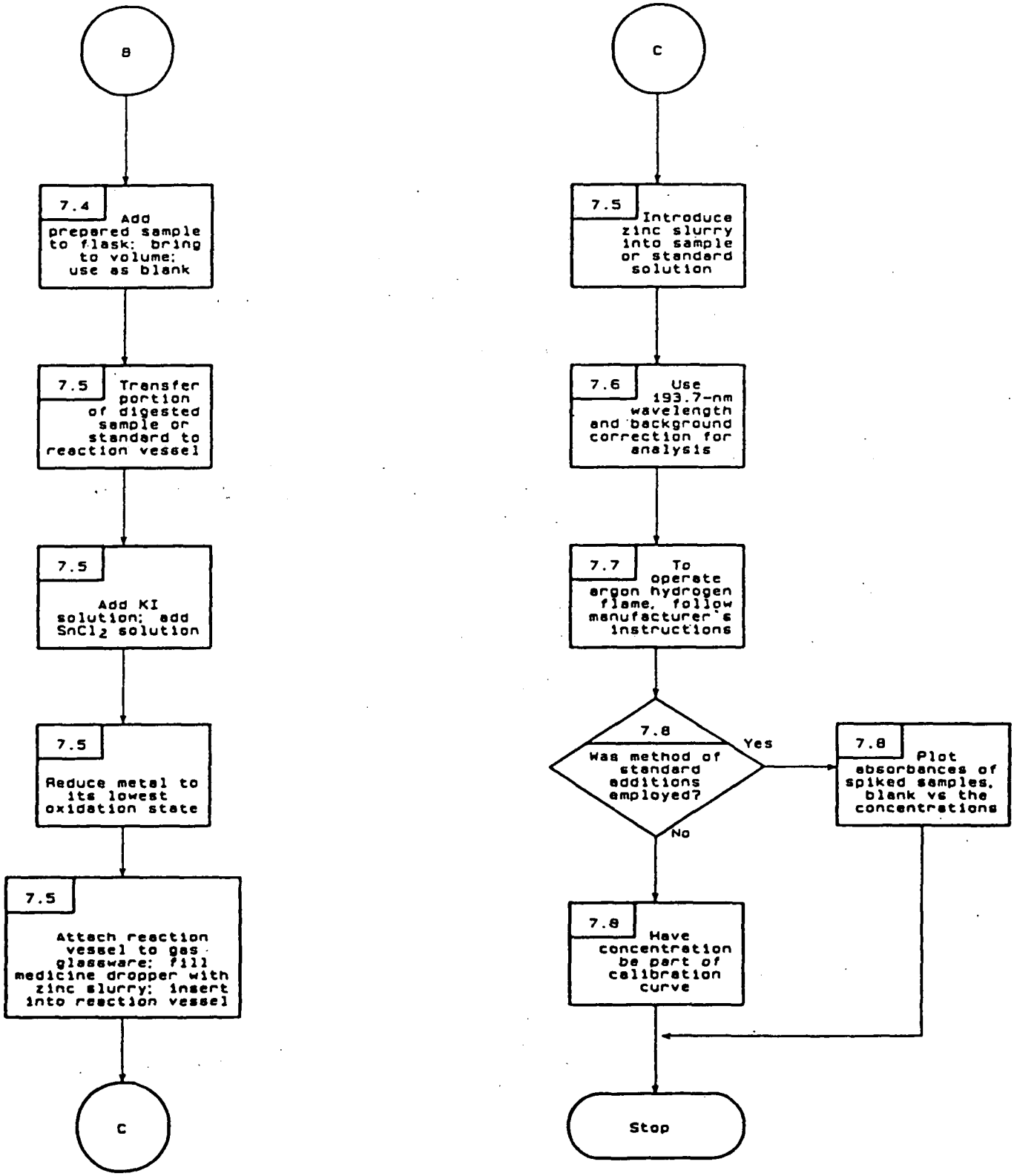
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 206.3 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods For Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.3.


Start
7.1
Place aliquot of digested sample in beaker
7.1
Add conc. HNO_3 and H_2SO_4; evaporate sample
7.1
Did sample char?
Yes
No
7.1
Turn off heat, cool, and add HNO_3
7.1
Continue adding HNO_3
A
A
7.1
When digestion is complete, cool sample; add Type II water; evaporate; cool
7.1
Transfer digested sample to flask; add conc. HCl; bring to volume
7.2
Prepare working standards; transfer to flasks; bring to volume
7.3
Are EP extracts analyzed, or is there matrix interference?
Yes
No
7.3
Take standards and transfer part of each to separate flasks; add prepared sample to each flask; bring to volume
B


B
7.4 Add prepared sample to flask; bring to volume; use as blank
7.5 Transfer portion of digested sample or standard to reaction vessel
7.5 Add KI solution; add $SnCl_2$ solution
7.5 Reduce metal to its lowest oxidation state
7.5 Attach reaction vessel to gas glassware; fill medicine dropper with zinc slurry; insert into reaction vessel
C
C
7.5 Introduce zinc slurry into sample or standard solution
7.6 Use 193.7-nm wavelength and background correction for analysis
7.7 To operate argon hydrogen flame, follow manufacturer's instructions
7.8 Was method of standard additions employed?
Yes
No
7.8 Plot absorbances of spiked samples, blank vs the concentrations
7.8 Have concentration be part of calibration curve
Stop

METHOD 7080

BARIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 High hollow cathode current settings and a narrow spectral band pass must be used, because both barium and calcium emit strongly at barium's analytical wavelength.

3.3 Barium undergoes significant ionization in the nitrous oxide/acetylene flame, resulting in a significant decrease in sensitivity. All samples and standards must contain 2 mL of the KCl ionization suppressant (Section 5.2.3 below) per 100 mL of solution.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Barium hollow cathode lamp.**
4.2.2 **Wavelength:** 553.6 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Nitrous oxide.
4.2.5 **Type of flame:** Fuel rich.
4.2.6 **Background correction:** Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.7787 g barium chloride ($BaCl_2 \cdot 2H_2O$, analytical reagent grade in Type II water and dilute to

1 liter. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing. All calibration standards and samples should contain 2 mL/100 mL of the potassium chloride (ionization suppressant) solution described in Section 5.2.3.

5.2.3 **Potassium chloride solution:** Dissolve 95 g potassium chloride (KCl) in Type II water and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

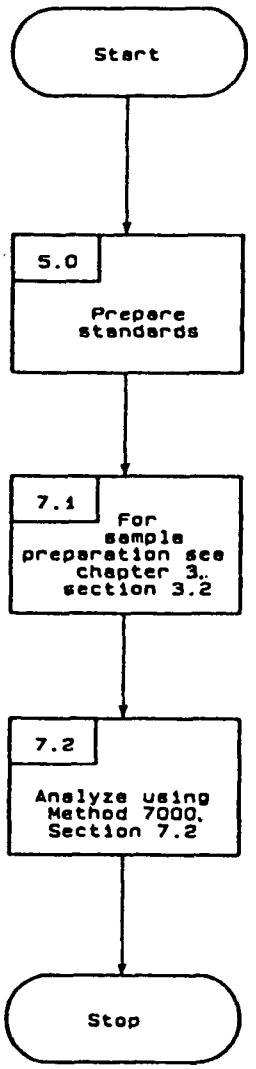
9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 1-20 mg/L with a wavelength of 553.6 nm.
Sensitivity: 0.4 mg/L.
Detection limit: 0.1 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 0.4 and 2 mg Ba/L gave standard deviations of $\pm$0.043 and $\pm$0.13, respectively. Recoveries at these levels were 94% and 113%, respectively.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 208.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7090

BERYLLIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction may be required because nonspecific absorption and light scattering can be significant at the analytical wavelength.

3.3 Concentrations of aluminum greater than 500 ppm may suppress beryllium absorbance. The addition of 0.1% fluoride has been found effective in eliminating this interference. High concentrations of magnesium and silicon cause similar problems and require the use of the method of standard additions.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Beryllium hollow cathode lamp.**
4.2.2 **Wavelength:** 234.9 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Nitrous oxide.
4.2.5 **Type of flame:** Fuel rich.
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 11.6586 g beryllium sulfate, $BeSO_4$, in Type II water containing 2 mL nitric acid and dilute to 1 liter.

Beryllium metal can also be dissolved in H_2SO_4. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample Preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

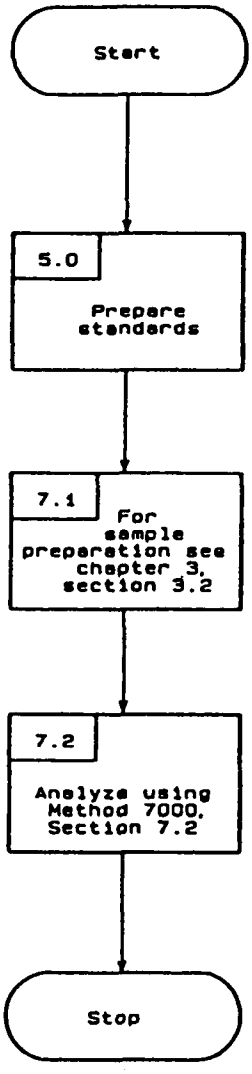
Optimum concentration range: 0.05-2 mg/L with a wavelength of 234.9 nm.
Sensitivity: 0.025 mg/L.
Detection limit: 0.005 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 0.01 and 0.25 mg/L gave standard deviations of $\pm$0.001 and $\pm$0.002, respectively. Recoveries at these levels were 100% and 97%, respectively.

9.3 For concentrations of beryllium below 0.02 mg/L, the furnace procedure (Method 7091) is recommended.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 210.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7091

BERYLLIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, beryllium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction is required to avoid erroneously high results.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Drying time and temp:** 30 sec at 125°C.
4.2.2 **Ashing time and temp:** 30 sec at 1000°C.
4.2.3 **Atomizing time and temp:** 10 sec at 2800°C.
4.2.4 **Purge gas:** Argon.
4.2.5 **Wavelength:** 234.9 nm.
4.2.6 **Background correction:** Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

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Date September 1986

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 11.6586 g beryllium sulfate, $BeSO_4$, in Type II water containing 2 mL concentrated nitric acid and dilute to 1 liter. Beryllium metal can also be dissolved in acid. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample Preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

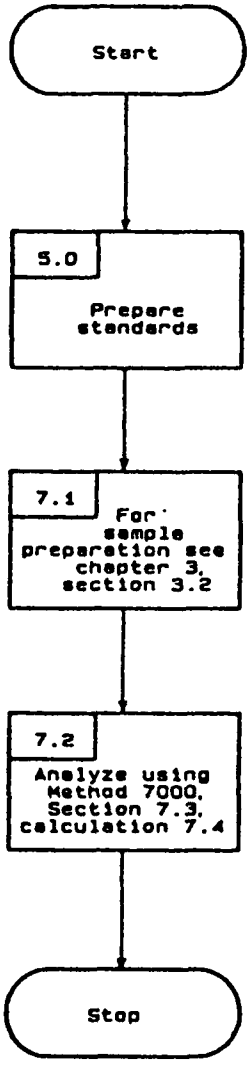
9.1 Precision and accuracy data are not available at this time.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 1-30 ug/L.
Detection limit: 0.2 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 210.2.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.3, calculation 7.4
Stop

METHOD 7130

CADMIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Nonspecific absorption and light scattering can be significant at the analytical wavelength. Thus background correction is required.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Cadmium hollow cathode lamp.**
4.2.2 **Wavelength:** 228.8 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Oxidizing (fuel lean).
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g cadmium metal (analytical reagent grade) in 20 mL of 1:1 HNO_3 and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same

concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.05-2 mg/L with a wavelength of 228.8 nm.
Sensitivity: 0.025 mg/L.
Detection limit: 0.005 mg/L.

9.2 For concentrations of cadmium below 0.02 mg/L, the furnace procedure (Method 7131) is recommended.

9.3 Precision and accuracy data are available in Method 213.1 of Methods for Chemical Analysis of Water and Wastes.

9.4 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

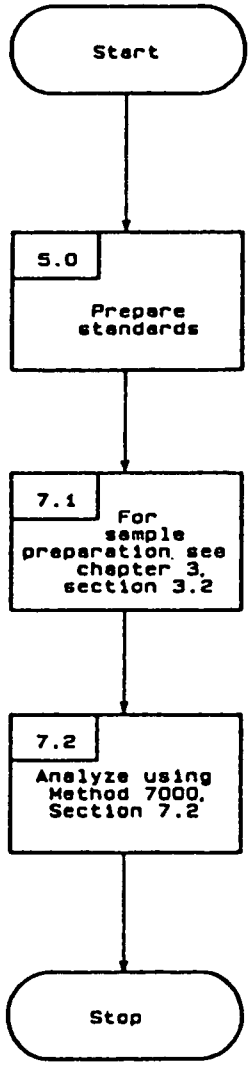
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 213.1.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	3050	2,770, 1,590 ug/g
Wastewater treatment sludge	3050	12,000, 13,000 ug/g


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7131

CADMIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, cadmium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction is required to avoid erroneously high results.

3.3 Excess chloride may cause premature volatilization of cadmium. Ammonium phosphate used as a matrix modifier minimizes this loss.

3.4 Many plastic pipet tips (yellow) contain cadmium. Use "cadmium-free" tips.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Drying time and temp:** 30 sec at 125°C.
4.2.2 **Ashing time and temp:** 30 sec at 500°C.
4.2.3 **Atomizing time and temp:** 10 sec at 1900°C.
4.2.4 **Purge gas:** Argon.
4.2.5 **Wavelength:** 228.8 nm.
4.2.6 **Background correction:** Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g of cadmium metal (analytical reagent grade) in 20 mL of 1:1 HNO_3 and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock cadmium solution to be used as **calibration standards** at the time of analysis. To each 100 mL of standard and sample alike add 2.0 mL of the ammonium phosphate solution. The calibration standards should be prepared to contain 0.5% (v/v) HNO_3.

5.2.3 **Ammonium phosphate solution** (40%): Dissolve 40 g of ammonium phosphate, $(NH_4)_2HPO_4$ (analytical reagent grade), in Type II water and dilute to 100 mL.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 213.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.5-10 ug/L.
Detection limit: 0.1 ug/L.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

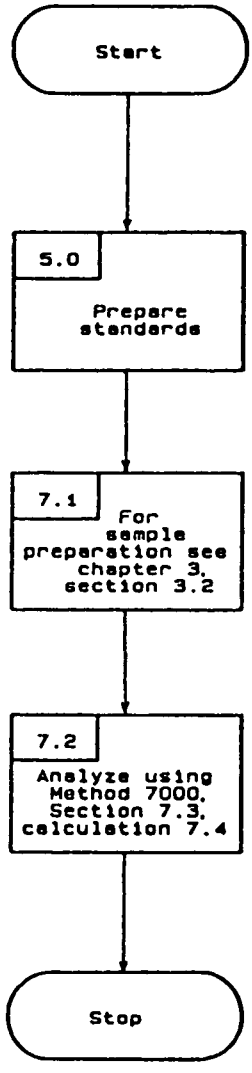
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 213.2.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Lagoon soil	3050	0.10, 0.095 ug/g
NBS SRM 1646 Estuarine sediment	3050	0.35 ug/g[a]
Solvent extract of oily waste	3030	1.39, 1.09 ug/L

[a]Bias of -3% from expected value.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.3, calculation 7.4
Stop

METHOD 7140

CALCIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000.

3.2 All elements forming stable oxyanions (P, B, Si, Cr, S, V, Ti, Al, etc.) will complex calcium and interfere unless lanthanum is added. Addition of lanthanum to prepared samples rarely presents a problem because virtually all environmental samples contain sufficient calcium to require dilution to be in the linear range of the method.

3.3 PO_4, SO_4, and Al are interferents. High concentrations of Mg, Na, and K interfere.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Calcium hollow cathode lamp.**
4.2.2 **Wavelength:** 422.7 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Nitrous oxide.
4.2.5 **Type of flame:** Stoichiometric.
4.2.6 **Background correction:** Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Suspend 2.500 g of $CaCO_3$ (analytical reagent grade, dried for 1 hr at 180°C) in Type II water and dissolve by adding a

minimum of dilute HCl. Dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing, including 1 mL of lanthanum chloride per 10 mL sample or standard (see Paragraph 5.2.3).

5.2.3 **Lanthanum chloride solution:** Dissolve 29 g La_2O_3 in 250 mL concentrated HCl -
CAUTION: REACTION IS VIOLENT -
and dilute to 500 mL with Type II water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

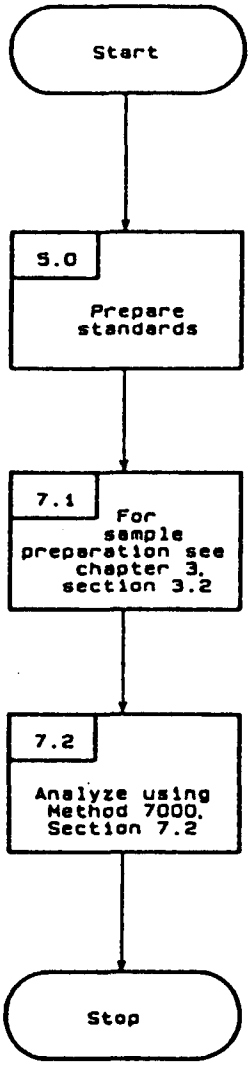
9.1 Precision and accuracy data are available in Method 215.1 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.2-7 mg/L with a wavelength of 422.7 nm.
Sensitivity: 0.08 mg/L.
Detection limit: 0.01 mg/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 215.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7190

CHROMIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 An ionization interference may occur if the samples have a significantly higher alkali metal content than the standards. If this interference is encountered, an ionization suppressant (KCl) should be added to both samples and standards.

3.3 Background correction may be required because nonspecific absorption and scattering can be significant at the analytical wavelength. Background correction with certain instruments may be difficult at this wavelength due to low-intensity output from hydrogen or deuterium lamps. Consult the specific instrument manufacturer's literature for details.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Chromium hollow cathode lamp.**
4.2.2 **Wavelength:** 357.9 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Nitrous oxide.
4.2.5 **Type of flame:** Fuel rich.
4.2.6 **Background correction:** Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.923 g of chromium trioxide (CrO_3, analytical reagent grade) in Type II water, acidify with redistilled HNO_3, and dilute to 1 liter. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.5-10 mg/L with a wavelength of 357.9 nm.
Sensitivity: 0.25 mg/L.
Detection limit: 0.05 mg/L.

9.2 For concentrations of chromium below 0.2 mg/L, the furnace procedure (Method 7191) is recommended.

9.3 Precision and accuracy data are available in Method 218.1 of Methods for Chemical Analysis of Water and Wastes.

9.4 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

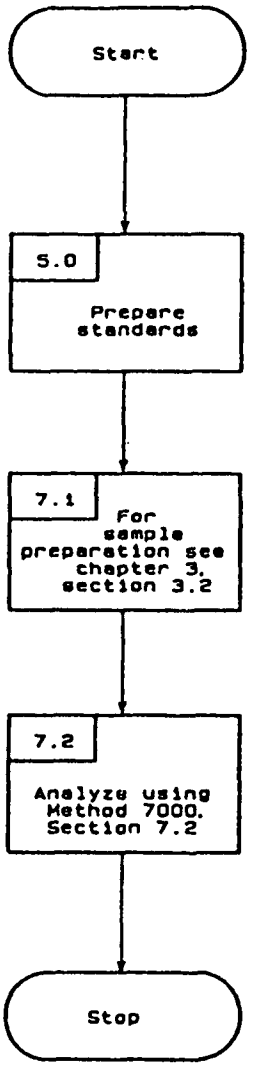
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.1.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	3050	6,100, 6,000 ug/g
Emission control dust	3050	2.0, 2.8 ug/g


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7191

CHROMIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Low concentrations of calcium and/or phosphate may cause interferences; at concentrations above 200 mg/L, calcium's effect is constant and eliminates the effect of phosphate. Calcium nitrate is therefore added to ensure a known constant effect.

3.3 Nitrogen should not be used as the purge gas because of a possible CN band interference.

3.4 Background correction may be required because nonspecific absorption and scattering can be significant at the analytical wavelength. Background correction with certain instruments may be difficult at this wavelength due to low-intensity output from hydrogen or deuterium lamps. Consult the specific instrument manufacturer's literature for details.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Drying time and temp:** 30 sec at 125°C.
4.2.2 **Ashing time and temp:** 30 sec at 1000°C.
4.2.3 **Atomizing time and temp:** 10 sec at 2700°C.
4.2.4 **Purge gas:** Argon (nitrogen should not be used).
4.2.5 **Wavelength:** 357.9 nm.
4.2.6 **Background correction:** Not required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection,

continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.923 g of chromium trioxide (CrO_3, analytical reagent grade) in Type II water, acidify with redistilled HNO_3, and dilute to 1 liter. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These standards should be prepared to contain 0.5% (v/v) HNO_3; 1 mL of 30% H_2O_2 and 1 mL of calcium nitrate solution, Section 5.2.3, may be added to lessen interferences (see Section 3.0).

5.2.3 **Calcium nitrate solution:** Dissolve 11.8 g of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade), in Type II water and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 218.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 5-100 ug/L.
Detection limit: 1 ug/L.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.2.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

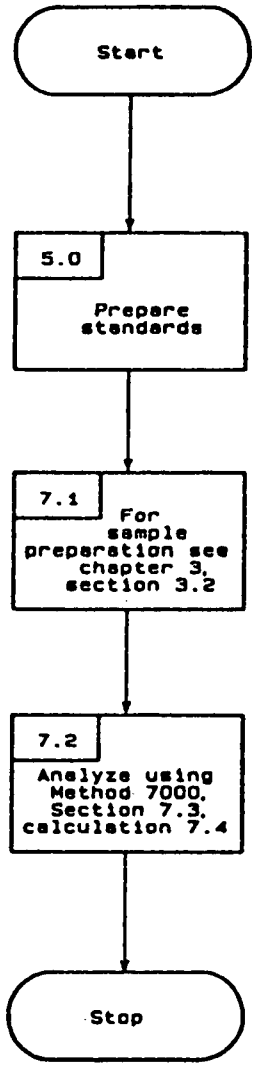
TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Paint primer	3050	2.7, 2.8 mg/g
Contaminated soil	3050	12.0, 12.3 ug/g
Oily lagoon soil	3050	69.6, 70.3 ug/g
NBS SRM 1646 Estuarine sediment	3050	42, 47 ug/g[a]
EPA QC Sludge	3050	156 ug/g[b]
NBS SRM 1085, Wear Metals in lubricating oil	3050	311, 356 ug/g[c]

[a]Bias of -45 and -38% from expected, respectively.

[b]Bias of -24% from expected.

[c]Bias of +4 and +19% from expected, respectively.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.3, calculation 7.4
Stop

METHOD 7195

CHROMIUM, HEXAVALENT (COPRECIPITATION)

1.0 SCOPE AND APPLICATION

1.1 Method 7195 is to be used to determine the concentration of dissolved hexavalent chromium [Cr(VI)] in Extraction Procedure (EP) toxicity characteristic extracts and ground waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present (see Paragraph 3.1 below).

1.2 Method 7195 may be used to analyze samples containing more than 5 ug of Cr(VI) per liter. Either flame or furnace atomic absorption spectroscopy (Methods 7190 and 7191) can be used with coprecipitation.

2.0 SUMMARY OF METHOD

2.1 Method 7195 is based on the separation of Cr(VI) from solution by coprecipitation of lead chromate with lead sulfate in a solution of acetic acid. After separation, the supernate [containing Cr(III)] is drawn off and the precipitate is washed to remove occluded Cr(III). The Cr(VI) is then reduced and resolubilized in nitric acid and quantified as Cr(III) by either flame or furnace atomic absorption spectroscopy (Methods 7190 and 7191).

3.0 INTERFERENCES

3.1 Extracts containing either sulfate or chloride in concentrations above 1,000 mg/L should be diluted prior to analysis.

4.0 APPARATUS AND MATERIALS

4.1 Filtering flask: Heavy wall, 1-liter capacity.

4.2 Centrifuge tubes: Heavy duty, conical, graduated, glass-stoppered, 10-mL capacity.

4.3 Pasteur pipets: Borosilicate glass, 6.8 cm.

4.4 Centrifuge: Any centrifuge capable of reaching 2,000 rpm and accepting the centrifuge tubes described in Section 4.2 may be used.

4.5 pH meter: A wide variety of instruments are commercially available and suitable for this work.

4.6 Test tube mixer: Any mixer capable of imparting a thorough vortex is acceptable.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Lead nitrate solution: Dissolve 33.1 g of lead nitrate, $Pb(NO_3)2$ (analytical reagent grade), in Type II water and dilute to 100 mL.

5.3 Ammonium sulfate solution: Dissolve 2.7 g of ammonium sulfate, $(NH_4)_2SO_4$ (analytical reagent grade), in Type II water and dilute to 100 mL.

5.4 Calcium nitrate solution: Dissolve 11.8 g of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade), in Type II water and dilute to 100 mL (1 mL = 20 mg Ca).

5.5 Nitric acid: Concentrated, distilled reagent grade or spectrograde quality.

5.6 Acetic acid, glacial, 10% (v/v): Dilute 10 mL glacial acetic acid, CH_3COOH (ACS reagent grade), to 100 mL with Type II water.

5.7 Ammonium hydroxide, 10% (v/v): Dilute 10 mL concentrated ammonium hydroxide, NH_4OH (analytical reagent grade), to 100 mL with Type II water.

5.8 Hydrogen peroxide, 30%: ACS reagent grade.

5.9 Potassium dichromate standard solution: Dissolve 28.285 g of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in Type II water and dilute to 1 liter (1 mL = 10 mg Cr).

5.10 Trivalent chromium working stock solution: To 50 mL of the potassium dichromate standard solution, add 1 mL of 30% H_2O_2 and 1 mL concentrated HNO_3 and dilute to 100 mL with Type II water (1 mL = 5.0 mg trivalent chromium). Prepare fresh monthly, or as needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Since the stability of Cr(VI) in EP extracts is not completely understood at this time, the analysis should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, samples and extracts should be stored at 4°C until analyzed. The maximum holding time prior to analysis is 24 hr.

7.0 PROCEDURE

7.1 Transfer a 50-mL portion of the sample to a 100-mL Griffin beaker and adjust to a pH of 3.5 ± 0.3 by adding volumes of 10% acetic acid dropwise. Proceed immediately to Step 7.2, taking no longer than 15 min between these steps.

NOTE: Care must be exercised not to take the pH below 3. If the pH is inadvertently lowered to <3, 10% NH_4OH should be used to readjust the pH to 3.5 ± 0.3.

7.2 Pipet a 10-mL aliquot of the adjusted sample into a centrifuge tube. Add 100 uL of the lead nitrate solution, stopper the tube, mix the sample, and allow to stand for 3 min.

7.3 After the formation of lead chromate, to help retain Cr(III) complex in solution, add 0.5 mL glacial acetic acid, stopper, and mix.

7.4 To provide adequate lead sulfate for coprecipitation, add 100 uL of ammonium sulfate solution, stopper, and mix.

7.5 Place the stoppered centrifuge tube in the centrifuge, making sure that the tube is properly counterbalanced. Start the centrifuge and slowly increase the speed to 2,000 rpm in small increments over a period of 5 min. Hold at 2,000 rpm for 1 min.

NOTE: The speed of the centrifuge must be increased slowly to ensure complete coprecipitation.

7.6 After centrifuging, remove the tube and withdraw and discard the supernate using either the apparatus detailed in Figure 1 or careful decantation. If using the vacuum apparatus, the pasteur pipet is lowered into the tube and the supernate is sucked over into the filtering flask. With care, the supernate can be withdrawn to within approximately 0.1 mL above the precipitate. Wash the precipitate with 5 mL Type II water and repeat steps 7.5 and 7.6; then proceed to 7.7.

7.7 To the remaining precipitate, add 0.5 mL concentrated HNO_3, 100 uL 30% H_2O_2, and 100 uL calcium nitrate solution. Stopper the tube and mix, using a vortex mixer to disrupt the precipitate and solubilize the lead chromate. Dilute to 10 mL, mix, and analyze in the same manner as the calibration standard.

7.8 Flame atomic absorption: At the time of analysis, prepare a blank and a series of at least four calibration standards from the Cr(III) working stock that will adequately bracket the sample and cover a concentration range of 1 to 10 mg Cr/L. Add to the blank and each standard, before diluting to final volume, 1 mL 30% H_2O_2, 5 mL concentrated HNO_3, and 1 mL calcium nitrate solution for each 100 mL of prepared solution. These calibration standards should be prepared fresh weekly, or as needed. Refer to Method 7090 for more detail.

7.9 Furnace atomic absorption: At the time of analysis, prepare a blank and a series of at least four calibration standards from the Cr(III) working stock that will adequately bracket the sample and cover a concentration range of 5 to 100 ug Cr/L. Add to the blank and each standard, before diluting to final volume, 1 mL 30% H_2O_2, 5 mL concentrated HNO_3, and 1 mL calcium nitrate solution for each 100 mL of prepared solution. These calibration standards should be prepared fresh weekly, or as needed. Refer to Method 7191 for more detail.

7.10 Verification:

7.10.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting precipitation. This must be accomplished by analyzing a second 10-mL aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. Under no circumstance should the increase be less than 30 ug/L Cr(VI). To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.10.2 If addition of the spike extends the concentration beyond the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

7.10.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed. If necessary, use furnace atomic absorption to achieve the optimal concentration range.

7.10.4 If the interference persists after sample dilution, an alternative method (Method 7197, Chelation/Extraction, or Method 7196, Colorimetric) should be used.

7.11 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), one can conclude that the analytical method has been verified.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

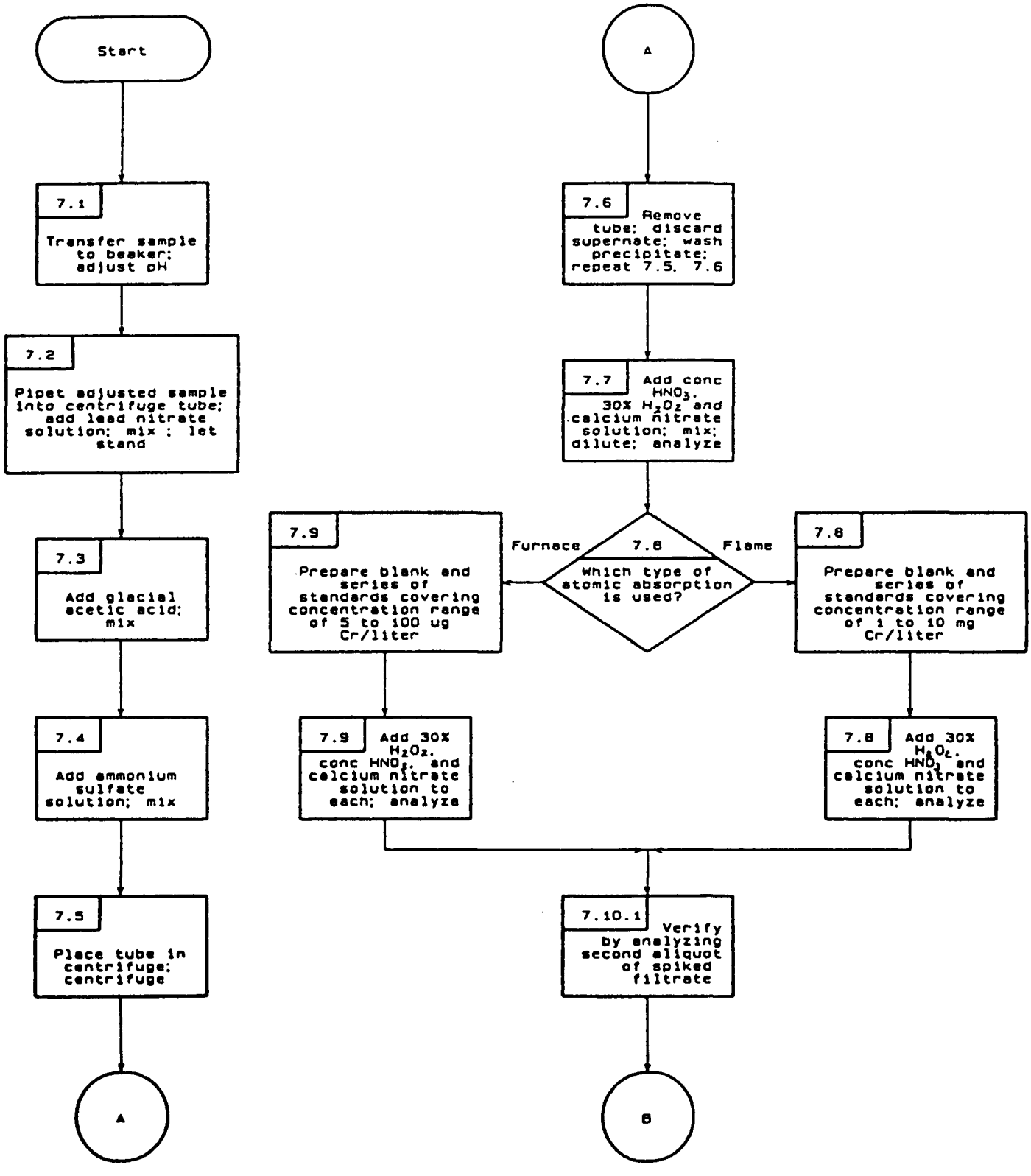
8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

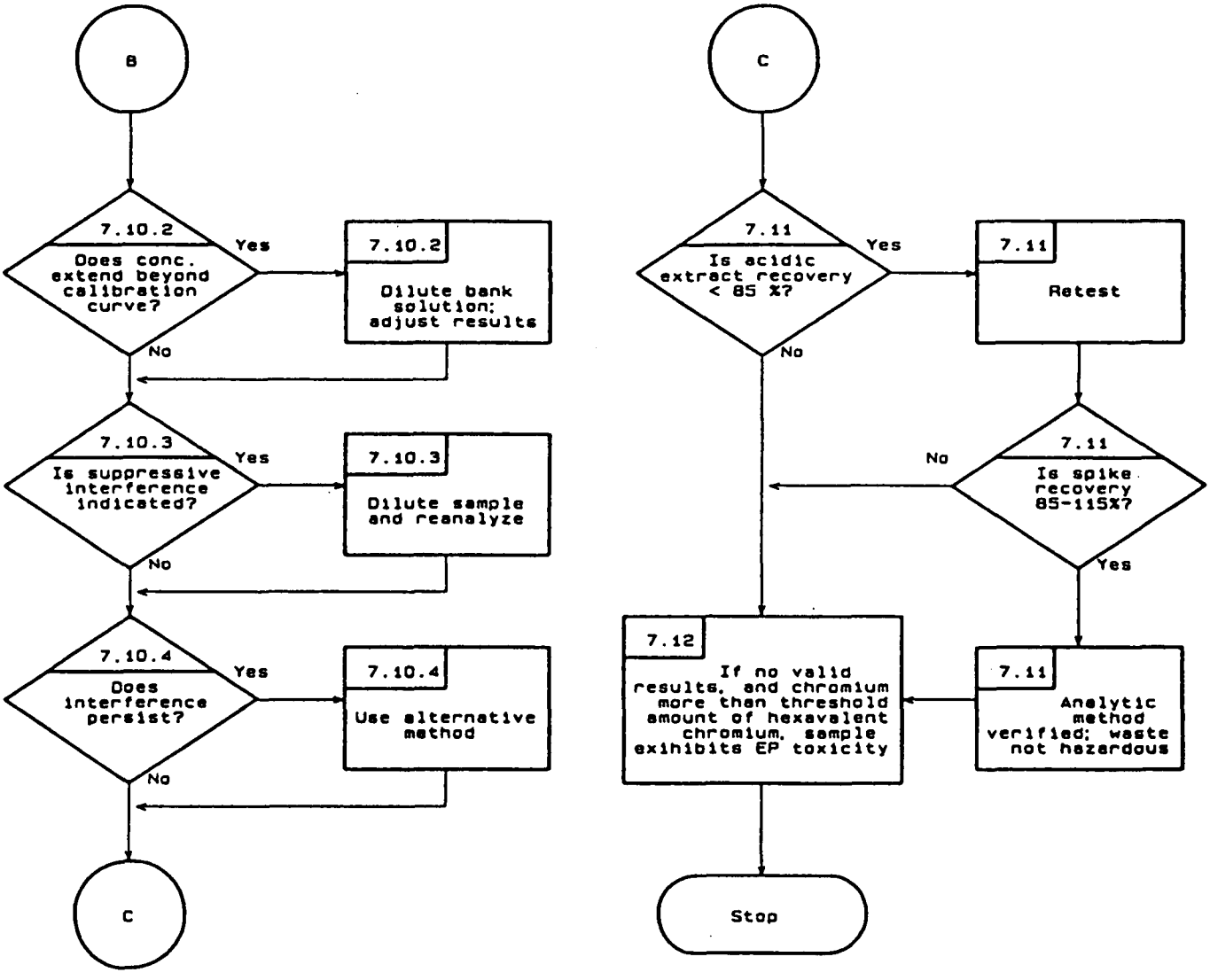
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 218.5 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.5.


Start
7.1
Transfer sample to beaker; adjust pH
7.2
Pipet adjusted sample into centrifuge tube; add lead nitrate solution; mix ; let stand
7.3
Add glacial acetic acid; mix
7.4
Add ammonium sulfate solution; mix
7.5
Place tube in centrifuge; centrifuge
A
A
7.6
Remove tube; discard supernate; wash precipitate; repeat 7.5, 7.6
7.7
Add conc HNO_3, 30% H_2O_2 and calcium nitrate solution; mix; dilute; analyze
7.8
Which type of atomic absorption is used?
Furnace
Flame
7.9
Prepare blank and series of standards covering concentration range of 5 to 100 ug Cr/liter
7.8
Prepare blank and series of standards covering concentration range of 1 to 10 mg Cr/liter
7.9
Add 30% H_2O_2, conc HNO_3, and calcium nitrate solution to each; analyze
7.8
Add 30% H_2O_2, conc HNO_3, and calcium nitrate solution to each; analyze
7.10.1
Verify by analyzing second aliquot of spiked filtrate
B


B
7.10.2
Does conc. extend beyond calibration curve?
Yes
7.10.2
Dilute bank solution; adjust results
No
7.10.3
Is suppressive interference indicated?
Yes
7.10.3
Dilute sample and reanalyze
No
7.10.4
Does interference persist?
Yes
7.10.4
Use alternative method
No
C
C
7.11
Is acidic extract recovery < 85 %?
Yes
7.11
Retest
No
7.11
Is spike recovery 85-115%?
No
Yes
7.12
If no valid results, and chromium more than threshold amount of hexavalent chromium, sample exihibits EP toxicity
7.11
Analytic method verified; waste not hazardous
Stop

METHOD 7196

CHROMIUM, HEXAVALENT (COLORIMETRIC)

1.0 SCOPE AND APPLICATION

1.1 Method 7196 is used to determine the concentration of dissolved hexavalent chromium [Cr(VI)] in Extraction Procedure (EP) toxicity characteristic extracts and ground waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present (see Paragraph 3.1 below).

1.2 Method 7196 may be used to analyze samples containing from 0.5 to 50 mg of Cr(VI) per liter.

2.0 SUMMARY OF METHOD

2.1 Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, may be determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red-violet color of unknown composition is produced. The reaction is very sensitive, the absorbancy index per gram atom of chromium being about 40,000 at 540 nm. Addition of an excess of diphenylcarbazide yields the red-violet product, and its absorbance is measured photometrically at 540 nm.

3.0 INTERFERENCES

3.1 The chromium reaction with diphenylcarbazide is usually free from interferences. However, certain substances may interfere if the chromium concentration is relatively low. Hexavalent molybdenum and mercury salts also react to form color with the reagent; however, the red-violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200 mg/L of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not cause trouble.

3.2 Iron in concentrations greater than 1 mg/L may produce a yellow color, but the ferric iron color is not strong and difficulty is not normally encountered if the absorbance is measured photometrically at the appropriate wavelength.

4.0 APPARATUS AND MATERIALS

4.1 Colorimetric equipment: One of the following is required: Either a spectrophotometer, for use at 540 nm, providing a light path of 1 cm or longer, or a filter photometer, providing a light path of 1 cm or longer and equipped with a greenish-yellow filter having maximum transmittance near 540 nm.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Potassium dichromate stock solution: Dissolve 141.4 mg of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in Type II water and dilute to 1 liter (1 mL = 50 ug Cr).

5.3 Potassium dichromate standard solution: Dilute 10.00 mL potassium dichromate stock solution to 100 mL (1 mL = 5 ug Cr).

5.4 Sulfuric acid, 10% (v/v): Dilute 10 mL of distilled reagent grade or spectrograde quality sulfuric acid, H_2SO_4, to 100 mL with Type II water.

5.5 Diphenylcarbazide solution: Dissolve 250 mg 1,5-diphenylcarbazide in 50 mL acetone. Store in a brown bottle. Discard when the solution becomes discolored.

5.6 Acetone (analytical reagent grade): Avoid or redistill material that comes in containers with metal or metal-lined caps.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Since the stability of Cr(VI) in EP extracts is not completely understood at this time, the analysis should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, the samples and extracts should be stored at 4°C until analyzed. The maximum holding time prior to analysis is 24 hr.

7.0 PROCEDURE

7.1 Color development and measurement: Transfer 95 mL of the extract to be tested to a 100-mL volumetric flask. Add 2.0 mL diphenylcarbazide solution and mix. Add H_2SO_4 solution to give a pH of 2 ± 0.5, dilute to 100 mL with Type II water, and let stand 5 to 10 min for full color development. Transfer an appropriate portion of the solution to a 1-cm absorption cell and measure its absorbance at 540 nm. Use Type II water as a reference. Correct the absorbance reading of the sample by subtracting the absorbance of a blank carried through the method (see Note below). An aliquot of the sample containing all reagents except diphenyl semicarbazide should be prepared and used to correct the sample for turbidity (i.e., a turbidity blank). From the

corrected absorbance, determine the mg/L of chromium present by reference to the calibration curve.

NOTE: If the solution is turbid after dilution to 100 mL in Step 7.1, above, take an absorbance reading before adding the carbazide reagent and correct the absorbance reading of the final colored solution by subtracting the absorbance measured previously.

7.2 Preparation of calibration curve:

7.2.1 To compensate for possible slight losses of chromium during digestion or other operations of the analysis, treat the chromium standards by the same procedure as the sample. Accordingly, pipet a chromium standard solution in measured volumes into 250-mL beakers or conical flasks to generate standard concentrations ranging from 0.5 to 5 mg/L Cr(VI) when diluted to the appropriate volume.

7.2.2 Develop the color of the standards as for the samples. Transfer a suitable portion of each colored solution to a 1-cm absorption cell and measure the absorbance at 540 nm. As reference, use Type II water. Correct the absorbance readings of the standards by subtracting the absorbance of a reagent blank carried through the method. Construct a calibration curve by plotting corrected absorbance values against mg/L of Cr(VI).

7.3 Verification:

7.3.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting color development. This must be accomplished by analyzing a second 10-mL aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. Under no circumstances should the increase be less than 30 g Cr(VI)/liter. To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.3.2 If addition of the spike extends the concentration beyond the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

7.3.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

7.3.4 If the interference persists after sample dilution, an alternative method (Method 7195, Coprecipitation, or Method 7197, Chelation/Extraction) should be used.

7.4 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is

obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), one can conclude that the analytical method has been verified..

7.5 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions (see Method 7000, Section 8.7).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.3 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.4 Verify calibration with an independently prepared check standard every 15 samples.

8.5 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

8.6 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

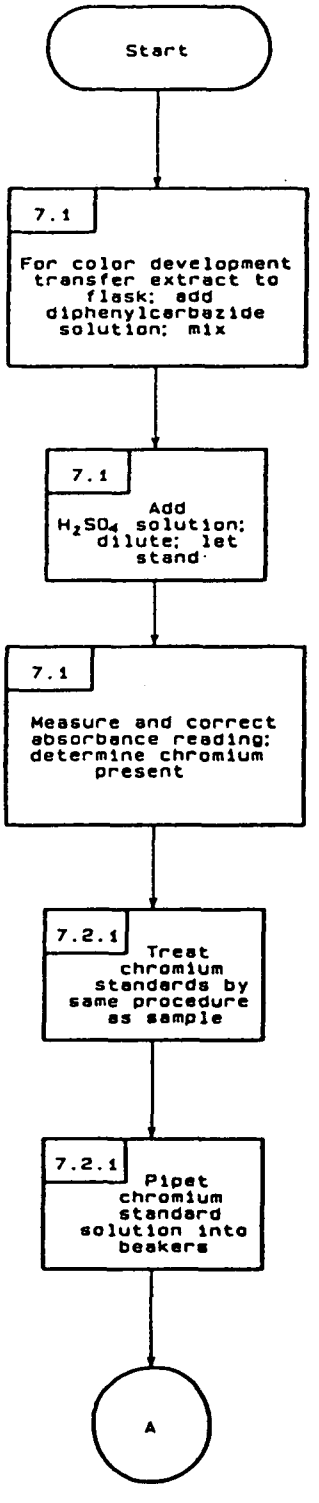
10.0 REFERENCES

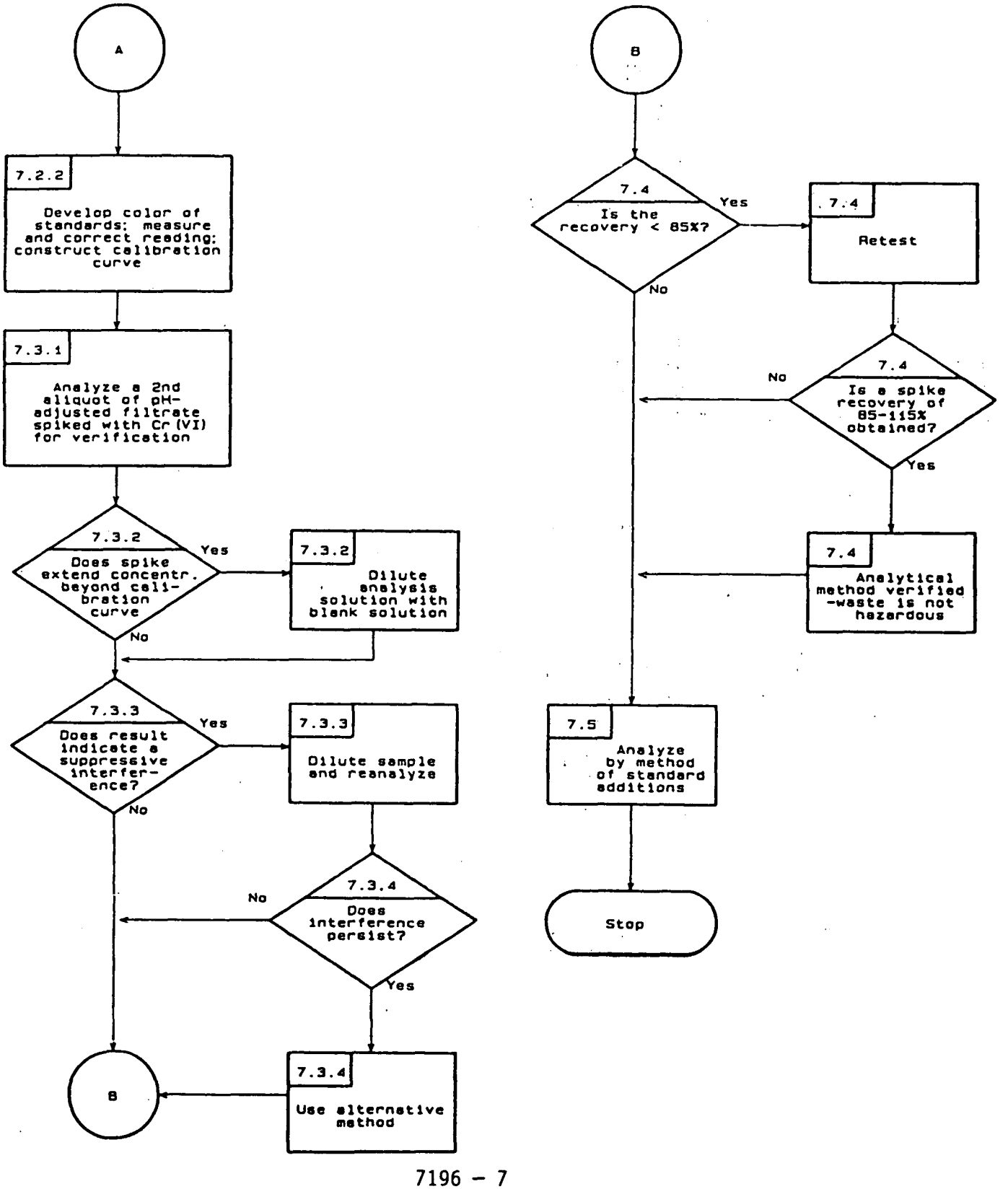
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Methods 218.4 and 218.5.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	Not known	0.096, 0.107 ug/g
Sediment from chemical storage area	3060	115, 117 ug/g


Start
7.1
For color development transfer extract to flask; add diphenylcarbazide solution; mix
7.1
Add H_2SO_4 solution; dilute; let stand
7.1
Measure and correct absorbance reading; determine chromium present
7.2.1
Treat chromium standards by same procedure as sample
7.2.1
Pipet chromium standard solution into beakers
A


A
7.2.2
Develop color of standards; measure and correct reading; construct calibration curve
7.3.1
Analyze a 2nd aliquot of pH-adjusted filtrate spiked with Cr(VI) for verification
7.3.2
Does spike extend concentr. beyond calibration curve
Yes
7.3.2
Dilute analysis solution with blank solution
No
7.3.3
Does result indicate a suppressive interference?
Yes
7.3.3
Dilute sample and reanalyze
No
7.3.4
Does interference persist?
No
Yes
7.3.4
Use alternative method
B
B
7.4
Is the recovery < 85%?
Yes
7.4
Retest
No
7.4
Is a spike recovery of 85-115% obtained?
No
Yes
7.4
Analytical method verified -waste is not hazardous
7.5
Analyze by method of standard additions
Stop

METHOD 7197

CHROMIUM, HEXAVALENT (CHELATION/EXTRACTION)

1.0 SCOPE AND APPLICATION

1.1 Method 7197 is approved for determining the concentration of dissolved hexavalent chromium [Cr(VI)] in Extraction Procedure (EP) toxicity characteristic extracts and ground waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present (see Paragraph 3.1).

1.2 Method 7197 may be used to analyze samples containing from 1.0 to 25 ug of Cr(VI) per liter.

2.0 SUMMARY OF METHOD

2.1 Method 7197 is based on the chelation of hexavalent chromium with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into the flame of an atomic absorption spectrophotometer.

3.0 INTERFERENCES

3.1 High concentrations of other metals may interfere.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Chromium hollow cathode lamp.

4.3 Strip-chart recorder (optional).

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Ammonium pyrrolidine dithiocarbamate (APDC) solution: Dissolve 1.0 g APDC in Type II water and dilute to 100 mL. Prepare fresh daily.

5.3 Bromphenol blue indicator solution: Dissolve 0.1 g bromphenol blue in 100 mL 50% ethanol.

5.4 Potassium dichromate standard solution I (1.0 mL = 100 ug Cr): Dissolve 0.2829 g pure dried potassium dichromate, $K_2Cr_2O_7$, in Type II water and dilute to 1,000 mL.

5.5 Potassium dichromate standard solution II (1.0 mL = 10.0 ug Cr): Dilute 100 mL chromium standard solution I to 1 liter with Type II water.

5.6 Potassium dichromate standard solution III (1.0 mL = 0.10 ug Cr): Dilute 10.0 mL chromium standard solution II to 1 liter with Type II water.

5.7 Methyl isobutyl ketone (MIBK), analytical reagent grade: Avoid or redistill material that comes in contact with metal or metal-lined caps.

5.8 Sodium hydroxide solution, 1 M: Dissolve to 40 g sodium hydroxide, NaOH (ASC reagent grade), in Type II water and dilute to 1 liter.

5.9 Sulfuric acid, 0.12 M: Slowly add 6.5 mL distilled reagent grade or spectrograde-quality sulfuric acid, H_2SO_4, to Type II water and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Because the stability of Cr(VI) in EP extracts is not completely understood at this time, the chelation and extraction should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, the samples and extracts should be stored at 4°C until analyzed.

7.0 PROCEDURE

7.1 Pipet a volume of extract containing less than 2.5 ug chromium (100 mL maximum) into a 200-mL volumetric flask and adjust the volume to approximately 100 mL.

7.2 Prepare a blank and sufficient standards and adjust the volume of each to approximately 100 mL.

7.3 Add 2 drops of bromphenol blue indicator solution. (The adjustment of pH to 2.4, Step 7.4, may be made with a pH meter instead of using an indicator.)

7.4 Adjust the pH by addition of 1 M NaOH solution dropwise until a blue color persists. Add 0.12 M H_2SO_4 dropwise until the blue color just disappears in both the standards and sample. Then add 2.0 mL of 0.12 M H_2SO_4 in excess. The pH at this point should be 2.4.

7.5 Add 5.0 mL APDC solution and mix. The pH should then be approximately 2.8.

7.6 Add 10.0 mL MIBK and shake vigorously for 3 min.

7.7 Allow the layers to separate and add Type II water until the ketone layer is completely in the neck of the flask.

7.8 Aspirate the ketone layer and record the scale reading for each sample and standard against the blank. Repeat, and average the duplicate results.

7.9 Determine the mg/liter of Cr(VI) in each sample from a plot of scale readings of standards. A working curve must be prepared with each set of samples.

7.10 Verification:

7.10.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting chelation. This must be accomplished by analyzing a second 10-mL aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. Under no circumstances should the increase be less than 30 ug/L Cr(VI). To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.10.2 If addition of the spike extends the concentration beyond the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

7.10.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

7.10.4 If the interference persists after sample dilution, an alternative method (Method 7195, Coprecipitation, or Method 7196, Colorimetric) should be used.

7.11 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), one can conclude that the analytical method has been verified.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

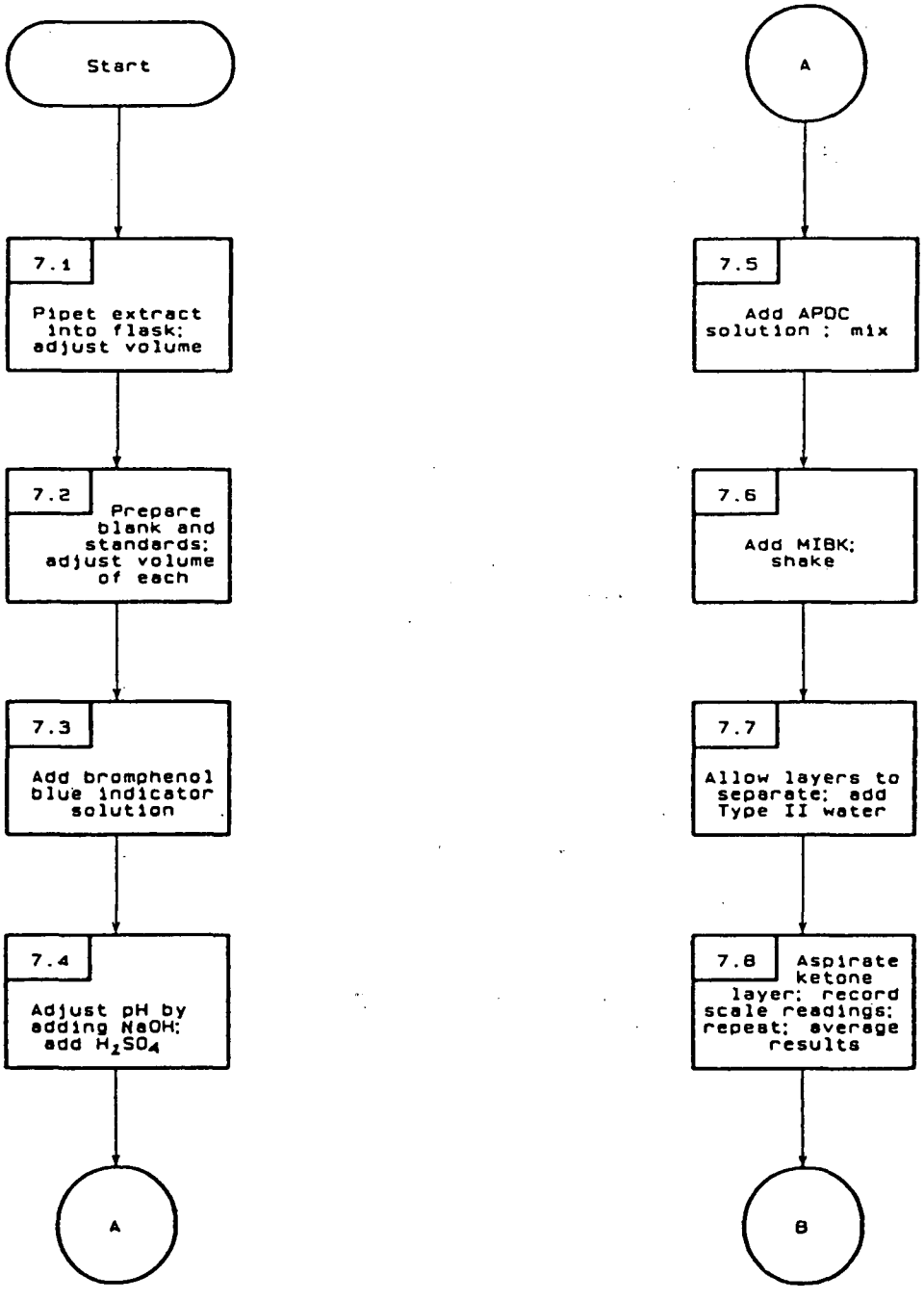
8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

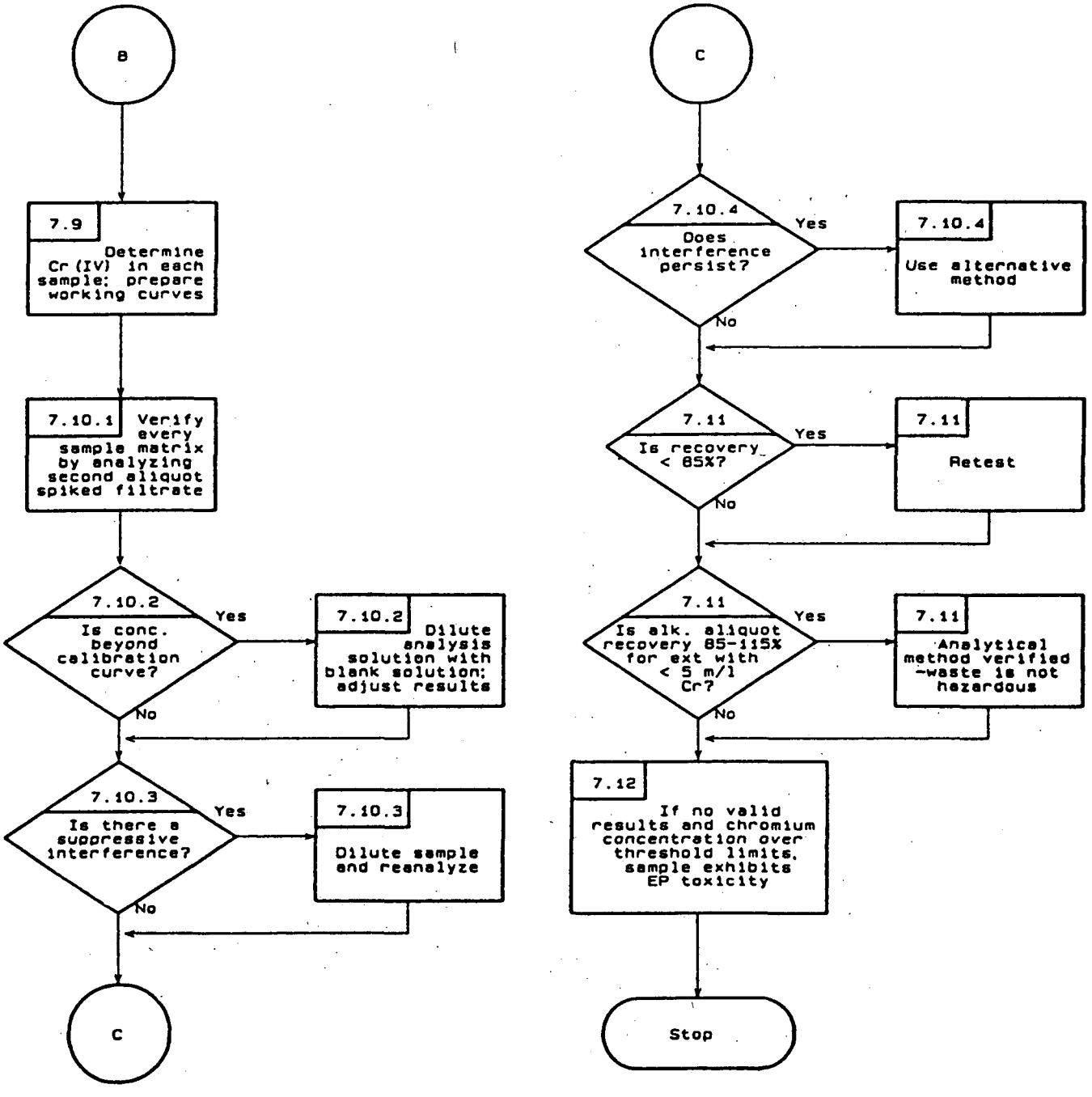
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 218.4 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.4.


Start
7.1
Pipet extract into flask; adjust volume
7.2
Prepare blank and standards; adjust volume of each
7.3
Add bromphenol blue indicator solution
7.4
Adjust pH by adding NaOH; add H_2SO_4
A
A
7.5
Add APDC solution ; mix
7.6
Add MIBK; shake
7.7
Allow layers to separate; add Type II water
7.8
Aspirate ketone layer; record scale readings; repeat; average results
B


B
7.9
Determine Cr(IV) in each sample; prepare working curves
7.10.1
Verify every sample matrix by analyzing second aliquot spiked filtrate
7.10.2
Is conc. beyond calibration curve?
Yes
7.10.2
Dilute analysis solution with blank solution; adjust results
No
7.10.3
Is there a suppressive interference?
Yes
7.10.3
Dilute sample and reanalyze
No
C
C
7.10.4
Does interference persist?
Yes
7.10.4
Use alternative method
No
7.11
Is recovery < 85%?
Yes
7.11
Retest
No
7.11
Is alk. aliquot recovery 85-115% for ext with < 5 m/l Cr?
Yes
7.11
Analytical method verified -waste is not hazardous
No
7.12
If no valid results and chromium concentration over threshold limits, sample exhibits EP toxicity
Stop

METHOD 7198

CHROMIUM, HEXAVALENT (DIFFERENTIAL PULSE POLAROGRAPHY)

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of hexavalent chromium [Cr(VI)] in natural and waste waters and in EP extracts.

1.2 The method can quantitate chromium in concentrations of up to 1.0 mg/L to 5.0 mg/L, depending on the mercury drop size. Higher concentrations can be determined by dilution.

1.3 The lower limit of detection for Cr(VI) is 10 ug/L for the instrumental conditions given in this method. The limit of detection could be easily lowered by changing these conditions.

2.0 SUMMARY OF METHOD

2.1 Method 7198 measures the peak current produced from the reduction of Cr(VI) to Cr(III) at a dropping mercury electrode during a differential pulse voltage ramp.

2.2 The method described herein uses 0.125 M NH_4OH-0.125 M NH_4Cl as the supporting electrolyte. In this electrolyte, Cr(VI) reduction results in peak current occurring at the peak potential (Ep) of -0.250 V vs. Ag/AgCl.

2.3 Alternative supporting electrolytes, such as those given in Table 1, may be used.

2.4 The technique of standard additions must be used to quantitate the Cr(VI) content.

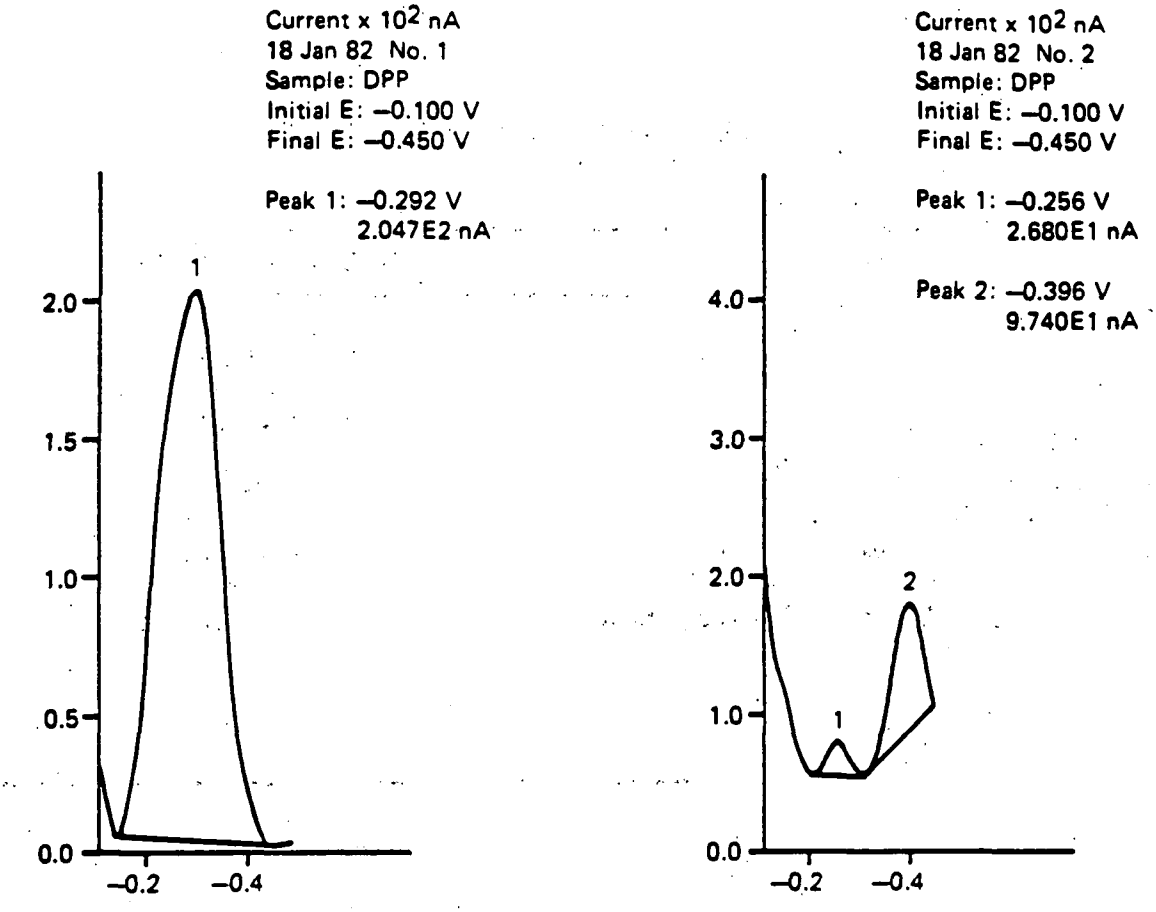
3.0 INTERFERENCES

3.1 Copper ion at concentrations higher than the Cr(VI) concentration is a potential interference due to peak overlap when using the 0.125 M ammoniacal electrolyte. Increasing the ammoniacal electrolyte concentration to 0.5 M shifts the copper peak cathodically (Ep = -0.4 V), eliminating the interference at a copper-to-chromium ratio of 10:1 (Figure 1).

3.2 Reductants such as ferrous iron, sulfite, and sulfide will reduce Cr(VI) to Cr(III); thus it is imperative to analyze the samples as soon as possible.

4.0 APPARATUS AND MATERIALS

4.1 Polarographic instrumentation: Capable of performing differential pulse analyses, including recorder or plotter.



A. 20 ppm Cu, 2.5 ppm Cr, 0.1 N buffer.

B. 20 ppm Cu, 2.5 ppm Cr, 0.5 N buffer.

Figure 1. Two polarograms illustrating shift in copper peak at higher ammoniacal electrolyte concentrations.

TABLE 1. POLAROGRAPHY OF HEXAVALENT CHROMIUM

Supporting electrolyte	Peak potential (vs. SCE)
1 M NaOH	-0.85
1 M Pyridine, 1 M NaOH	-1.48
1 M NH_4OH, 1 M NH_4Cl	-0.36
0.1 M NH_4OH, 0.1 M $(NH_4)_2$ Tartrate	-0.244
0.2 M KCl, 0.3 M Triethanolamine, pH 9	-0.28
1 M Na_2SO_4	-0.23
0.1 M NH_4OH, 0.1 M NH_4Cl	-0.25

4.2 Dropping mercury electrode assembly: Capable of performing differential pulse analyses.

4.3 Counter electrode: Platinum wire.

4.4 Reference electrode: Ag/AgCl or SCE, with a slow-leakage fritted tip (unfired Vycor).

4.5 Nitrogen gas and cell outgassing assembly.

4.6 Micropipets and disposable tips.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Chromium standard solution I, 1.0 mL = 100 ug Cr: Should be made daily from a 1,000-ppm standard stock solution made with Type II water.

5.3 Chromium standard solution II, 1.0 mL = 10 ug Cr: Should be made daily from a 1,000-ppm standard stock solution made with Type II water.

5.4 Chromium standard solution III, 1.0 mL = 1 ug Cr: Dilute 10 mL chromium standard solution II to 100 mL with Type II water.

5.5 Ammoniacal electrolyte, 2.5 N: Dissolve 33.3 g of NH_4Cl in 150 mL of Type II water, add 42.2 mL of concentrated NH_4OH, and dilute to 250 mL.

5.6 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Stability of Cr(VI) is not completely understood at this time. Therefore, the analysis should be carried out as soon as possible.

6.3 If the analysis cannot be performed within 24 hr, take an aliquot of the sample and add a known amount of Cr(VI) (0.1 mg/L for natural waters, 1 mg/L for wastewaters, and 5 mg/L for EP extracts). Analyze this known additional sample at the same time the sample is analyzed to determine whether Cr(VI) was reduced during storage.

6.4 To retard the chemical activity of Cr(VI), the sample should be transported and stored at 4°C until time of analysis.

7.0 PROCEDURE

7.1 Soak the voltammetric cells overnight in 1 + 1 HNO_3 and/or 1 + 1 aqua regia.

7.2 Rinse the electrode assembly with Type II water, then with 1 N HNO_3, and finally with Type II water prior to and in between sample analyses.

7.3 The instrument should be set using the following instrumental parameters.

7.3.1 **Mode:** Differential pulse.
7.3.2 **Scan rate:** 2 mV/sec.
7.3.3 **Drop time:** 1 sec.
7.3.4 **Initial potential:** -0.05 V $\pm$ 0.05 V vs. Ag/AgCl.
7.3.5 **Final potential:** -0.50 V $\pm$ 0.10 V vs. Ag/AgCl.
7.3.6 **Pulse height:** 0.05 V.
7.3.7 **Deaeration time:** 240 sec or less initially, 30 sec between standard additions.

7.4 Analysis:

7.4.1 Pipet a volume of sample containing less than 10 ug Cr(VI) into a voltammetric cell (the maximum volume depends on the voltammetric cell volume, usually 10 mL).

7.4.2 Add 0.5 mL of the ammoniacal electrolyte and adjust volume to 10 mL with Type II water.

7.4.3 Place the electrode assembly in the solution and outgas with nitrogen for at least 120 sec.

7.4.4 Engage the electrode assembly to the polarographic analyzer and displace at least 10 mercury drops before initiating the voltage ramp and obtaining the polarogram.

7.4.5 Figure 2 gives typical differential pulse polarograms.

7.5 Prior to the analysis of any samples, and during analysis at a frequency of at least once every 10 samples, verify that the cell contamination is less than 10 ug/L Cr by analyzing demineralized water and the appropriate volume of supporting electrolyte in a manner similar to the procedure described in 7.4.3 and 7.4.4.

7.6 Calibration:

7.6.1 After running a differential pulse polarogram on the sample solution, quantitate the chromium using the technique of standard addition.

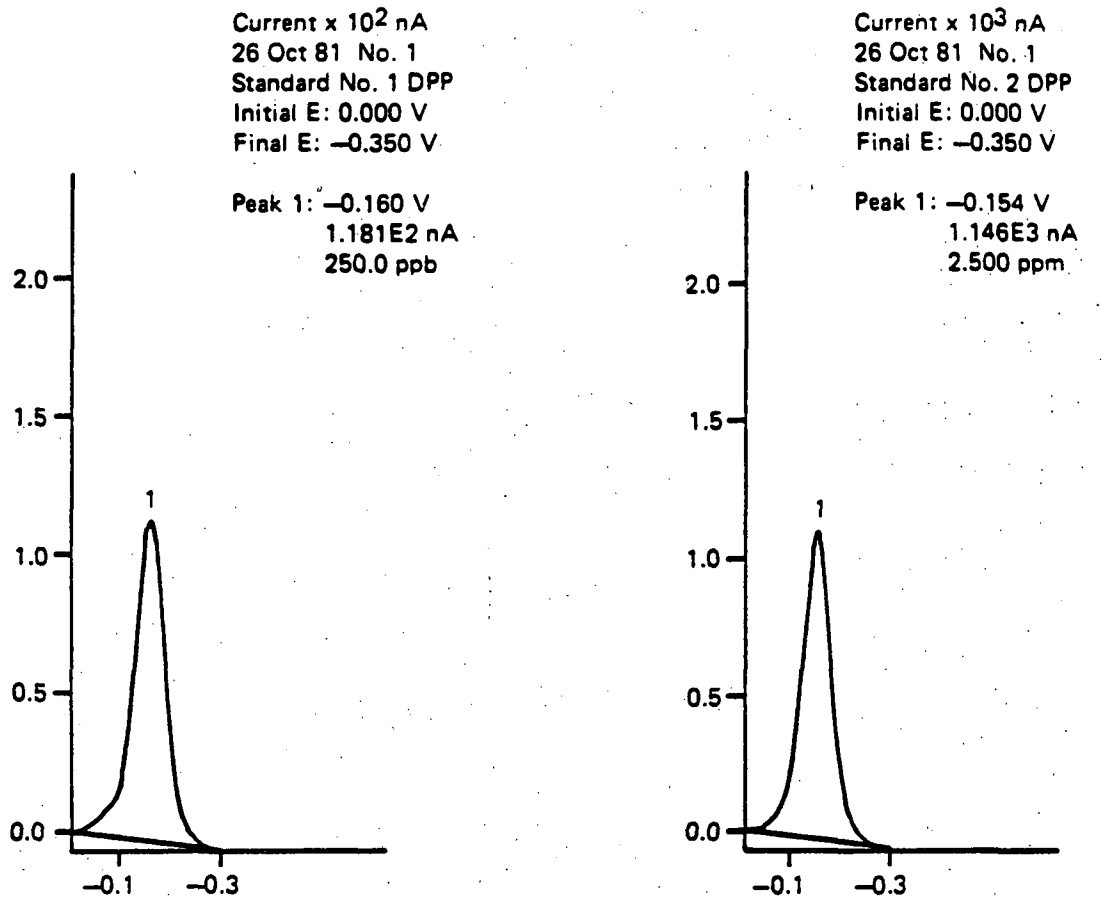


Figure 2. Typical differential pulse polarogram at 0.25 ppm and 2.5 ppm Cr in 0.1 N buffer.

7.6.2 Three standard additions should be made to obtain the best precision and accuracy. The first standard addition should be approximately one-half the concentration of the sample, the second equal to that of the sample, and the third about 1.5 times the sample concentration. The total volume due to standard additions should not exceed the cell value by more than 10%.

7.6.3 Add an appropriate aliquot of chromium standard solution I, II, or III to the sample in the cell. Deaerate for 30 sec to mix the solution and remove oxygen added with the known addition.

7.6.4 Repeat the analysis procedure, beginning with Step 7.4.4 for each standard addition.

7.7 Calculations:

7.7.1 Calculate the concentration of chromium determined by each standard addition procedure as follows:

$$C_u = \frac{i_1 V_i C_s}{i_1 V_i + (i_1 - i_1)V} \times \frac{V}{V_u}$$

where:

i_1 = Current peak height for the sample (nA);

i_i = Current peak height for the sample plus standard (nA);

V_u = Volume of sample in the cell (mL);

V_i = Volume of standard taken for spiking (mL);

V = Volume in cell prior to standard addition;

C_s = Concentration of standard used to spike (mg/L); and

C_u = Concentration of the unknown in the sample (mg/L).

7.7.2 Some microprocessor polarographic systems will perform these calculations automatically.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 If necessary, dilute samples so that they fall within the working range.

8.3 Quantitation must be performed by the method of standard additions (see Method 7000, Section 8.7).

8.4 Verify calibration with an independently prepared check standard every 15 samples (see Chapter One, Section 1.1.8).

8.5 Standards should be compared to a reference standard on a routine basis.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data for this method are summarized in Table 2.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.4 and 218.5.

TABLE 2. PRECISION AND ACCURACY OF THE DPP OF HEXAVALENT CHROMIUM

2a. Precision

Sample type	No. of replicates	Average value	% RSD
Leachate[a]	3	1.87	0.69

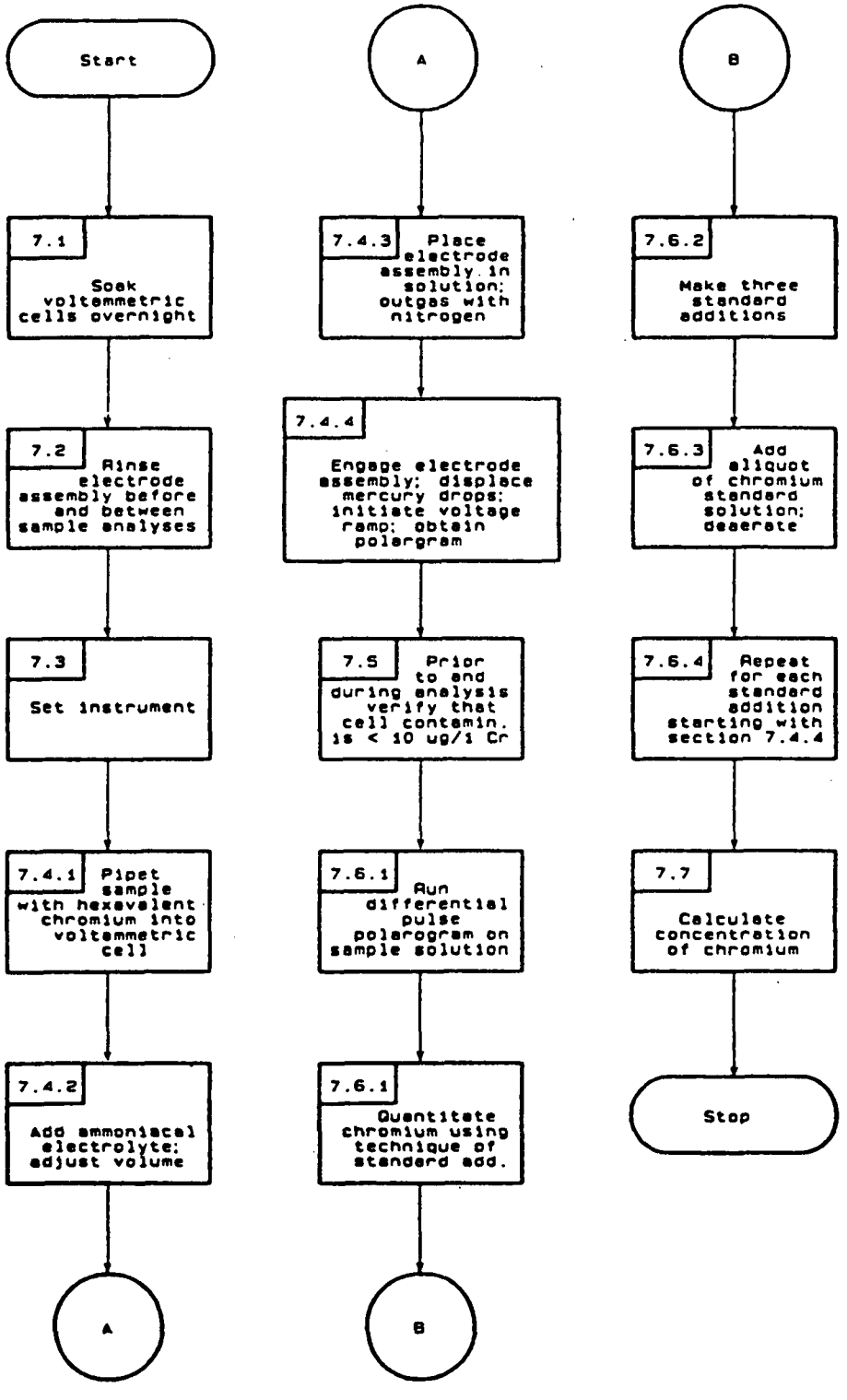
2b. Accuracy (spike recovery data)

Sample type	Spike level (mg/L)	No. of samples	Average % recovery	Standard deviation of % recovery
EP extracts	5.0	8	92.8	6.4

2c. Methods comparison

	Diff. pulse polarography	APDC extraction ICAP-OES	Ion chromatography coupled to ICAP-OES
Value[a]	1.87	1.84	1.91

[a]Leachate sample from a waste disposal site.


Start
7.1 Soak voltammetric cells overnight
7.2 Rinse electrode assembly before and between sample analyses
7.3 Set instrument
7.4.1 Pipet sample with hexavalent chromium into voltammetric cell
7.4.2 Add ammoniacal electrolyte; adjust volume
A
A
7.4.3 Place electrode assembly in solution; outgas with nitrogen
7.4.4 Engage electrode assembly; displace mercury drops; initiate voltage ramp; obtain polergram
7.5 Prior to and during analysis verify that cell contamin. is < 10 ug/l Cr
7.6.1 Run differential pulse polerogram on sample solution
7.6.1 Quantitate chromium using technique of standard add.
B
B
7.6.2 Make three standard additions
7.6.3 Add aliquot of chromium standard solution; deaerate
7.6.4 Repeat for each standard addition starting with section 7.4.4
7.7 Calculate concentration of chromium
Stop

METHOD 7200

COBALT (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Excesses of other transition metals may slightly depress the response of cobalt. Matrix matching or the method of standard additions is recommended.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Cobalt hollow cathode lamp.**
4.2.2 **Wavelength:** 240.7 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Oxidizing (fuel lean).
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g of cobalt metal (analytical reagent grade) in 20 mL of 1:1 HNO_3 and dilute to 1 liter with Type II water. Chloride or nitrate salts of cobalt (II) may be used. Although numerous hydrated forms exist, they are not recommended unless the exact composition of the compound is known. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

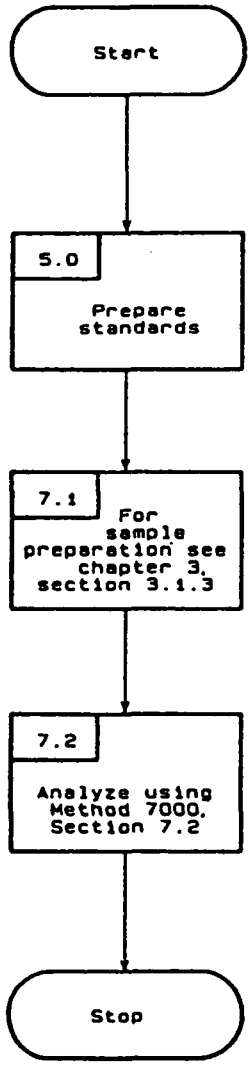
Optimum concentration range: 0.5-5 mg/L with a wavelength of 240.7 nm.
Sensitivity: 0.2 mg/L.
Detection limit: 0.05 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 0.2, 1, and 5 mg/L gave standard deviations of $\pm$0.013, $\pm$0.01, and $\pm$0.05, respectively. Recoveries at these levels were 98% and 97%, respectively.

9.3 For concentrations of cobalt below 0.1 mg/L, the furnace procedure (Method 7201) is recommended.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 219.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.1.3
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7201

COBALT (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Excess chloride may interfere. It is necessary to verify by standard additions that the interference is absent.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Drying time and temp:** 30 sec at 125°C.
4.2.2 **Ashing time and temp:** 30 sec at 900°C.
4.2.3 **Atomizing time and temp:** 10 sec at 2700°C.
4.2.4 **Purge gas:** Argon.
4.2.5 **Wavelength:** 240.7 nm.
4.2.6 **Background correction:** Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g of cobalt metal (analytical reagent grade) in 20 mL of 1:1 HNO_3 and dilute to 1 liter with Type II water. Chloride or nitrate salts of cobalt (II) may be used. Although numerous hydrated forms exist, they are not recommended unless the exact composition of the compound is known. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

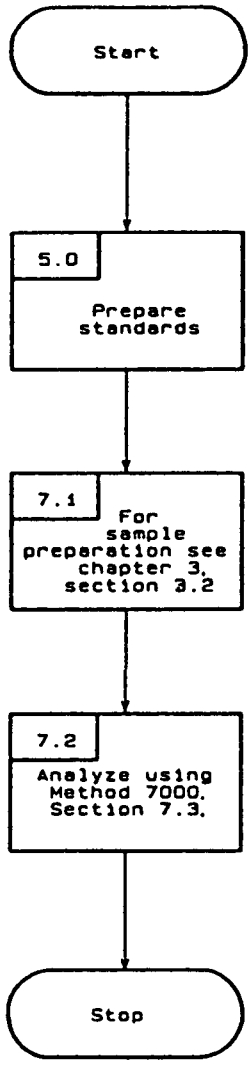
9.1 Precision and accuracy data are not available at this time.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 5-100 ug/L.
Detection limit: 1 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 219.2.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.3.
Stop

METHOD 7210

COPPER (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000.

3.2 Background correction may be required because nonspecific absorption and scattering can be significant at the analytical wavelength. Background correction with certain instruments may be difficult at this wavelength due to low-intensity output from hydrogen or deuterium lamps. Consult specific instrument manufacturer's literature for details.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Copper hollow cathode lamp.**
4.2.2 **Wavelength:** 324.7 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Oxidizing (fuel lean).
4.2.6 **Background correction:** Recommended, if possible.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.00 g of electrolytic copper (analytical reagent grade) in 5 mL of redistilled HNO_3 and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

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5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

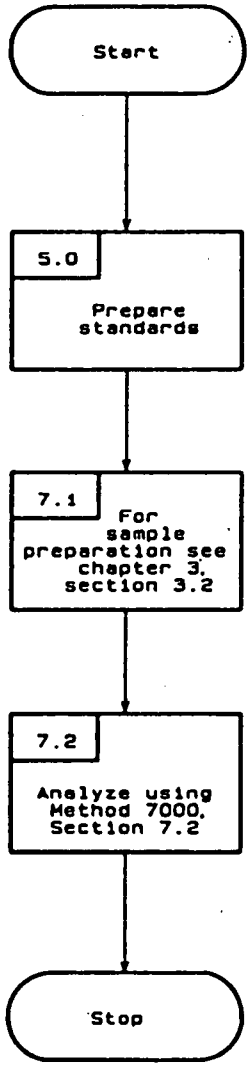
9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.2-5 mg/L with a wavelength of 324.7 nm.
Sensitivity: 0.1 mg/L.
Detection limit: 0.02 mg/L.

9.2 Precision and accuracy data are available in Method 220.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 220.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7380

IRON (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Iron is a universal contaminant, and great care should be taken to avoid contamination.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Iron hollow cathode lamp.**
4.2.2 **Wavelength:** 248.3 nm (primary); 248.8, 271.9, 302.1, 252.7, or 372.0 nm (alternates).
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Oxidizing (fuel lean).
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g iron wire (analytical reagent grade) in 10 mL redistilled HNO_3 and Type II water and dilute to 1 liter with Type II water. Note that iron passivates in concentrated HNO_3, and thus some water should be present. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

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5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

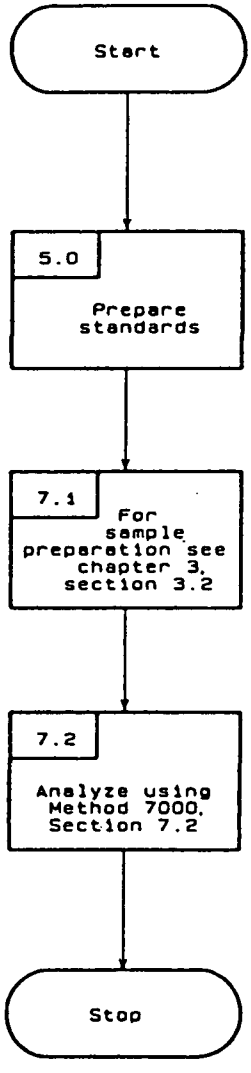
9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.3-5 mg/L with a wavelength of 248.3 nm.
Sensitivity: 0.12 mg/L.
Detection limit: 0.03 mg/L.

9.2 Precision and accuracy data are available in Method 236.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 236.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7420

LEAD (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction is required at either wavelength.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Lead hollow cathode lamp.**
4.2.2 **Wavelength:** 283.3 nm (primary); 217.0 nm (alternate).
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Oxidizing (fuel lean).
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.599 g of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), in Type II water, acidify with 10 mL redistilled HNO_3, and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 1-20 mg/L with a wavelength of 283.3 nm.
Sensitivity: 0.5 mg/L.
Detection limit: 0.1 mg/L.

9.2 For concentrations of lead below 0.2 mg/L, the furnace technique (Method 7421) is recommended.

9.3 Precision and accuracy data are available in Method 239.1 of Methods for Chemical Analysis of Water and Wastes.

9.4 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

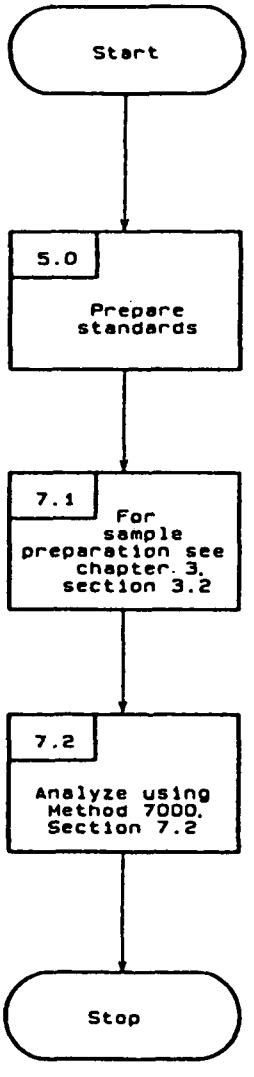
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 239.1.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	3050	450, 404 ug/g
Emission control dust	3050	42,500, 63,600 ug/g


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7421

LEAD (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction is required.

3.3 If poor recoveries are obtained, a matrix modifier may be necessary. Add 10 uL of phosphoric acid (Paragraph 5.3) to 1 mL of prepared sample in the furnace sampler cup and mix well.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Drying time and temp:** 30°sec at 125°C.
4.2.2 **Ashing time and temp:** 30°sec at 500°C.
4.2.3 **Atomizing time and temp:** 10 sec at 2700°C.
4.2.4 **Purge gas:** Argon.
4.2.5 **Wavelength:** 283.3 nm.
4.2.6 **Background correction:** Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.599 g of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), in Type II water, acidify with 10 mL redistilled HNO_3, and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing (0.5% v/v HNO_3).

5.3 Phosphoric acid: Reagent grade.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 239.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 5-100 ug/L.
Detection limit: 1 ug/L.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

1. Lead by Flameless Atomic Absorption with Phosphate Matrix Modification, Atomic Spectroscopy, 1 (1980), no. 3, pp. 80-81.

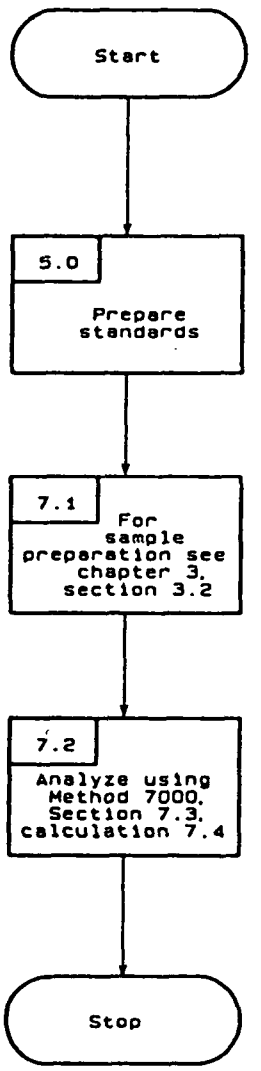
2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Contaminated soil	3050	163, 120 mg/g
Paint primer	3050	0.55, 0.63 mg/g
Lagoon soil	3050	10.1, 10.0 ug/g
NBS SRM 1646 Estuarine sediment	3050	23.7 ug/g[a]
NBS SRM 1085 Wear metals in lubricating oil	3030	274, 298 ug/g[b]
Solvent extracted oily waste	3030	9, 18 ug/L

[a]Bias of -16% from expected.

[b]Bias of -10 and -2% from expected, respectively.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.3, calculation 7.4
Stop

METHOD 7450

MAGNESIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 All elements forming stable oxyanions (P, B, Si, Cr, S, V, Ti, Al, etc.) will complex magnesium and interfere unless lanthanum is added. (See Method 7000, Paragraph 3.1.1.) Addition of lanthanum to prepared samples rarely presents a problem because virtually all environmental samples contain sufficient magnesium to require dilution to be in the linear range of the method.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Magnesium hollow cathode lamp.**
4.2.2 **Wavelength:** 285.2 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Oxidizing (fuel lean).
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g of magnesium metal (analytical reagent grade) in 20 mL 1:1 HNO_3 and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing, including 1 mL lanthanum solution per 10 mL solution (see Paragraph 3.2).

5.2.3 **Lanthanum chloride solution:** Dissolve 29 g La_2O_3 in 250 mL concentrated HCl -
(CAUTION: REACTION IS VIOLENT!) -
and dilute to 500 mL with Type II water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

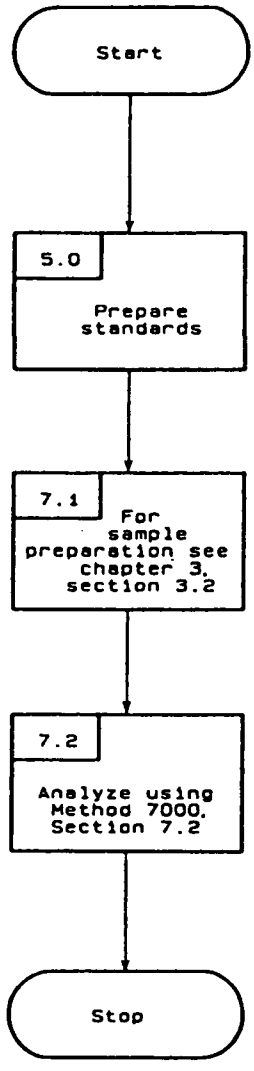
9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.02-0.05 mg/L with a wavelength of 285.2 nm.
Sensitivity: 0.007 mg/L.
Detection limit: 0.001 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 2.1 and 8.2 mg/L gave standard deviations of $\pm$0.1 and $\pm$0.2, respectively. Recoveries at both of these levels were 100%.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 242.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7460

MANGANESE (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction is required.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Manganese hollow cathode lamp.**
4.2.2 **Wavelength:** 279.5 nm (primary); 403.1 nm (alternate).
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Slightly oxidizing (slightly fuel-lean to stoichiometric).
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g manganese metal (analytical reagent grade) in 10 mL redistilled HNO_3 and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

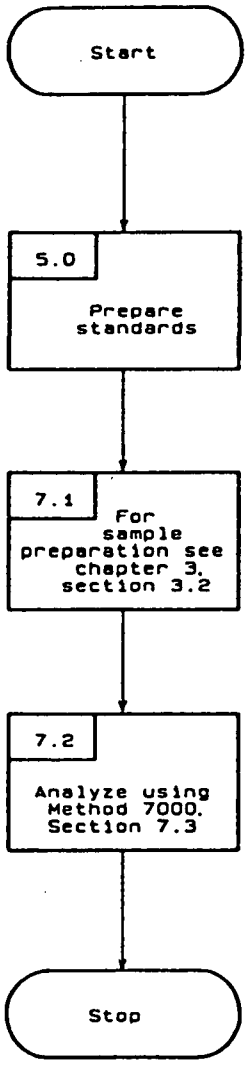
9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.1-3 mg/L with a wavelength of 279.5 nm.
Sensitivity: 0.05 mg/L.
Detection limit: 0.01 mg/L.

9.2 Precision and accuracy data are available in Method 243.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 243.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.3
Stop

METHOD 7470

MERCURY IN LIQUID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7470 is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters. (Method 7470 can also be used for analyzing certain solid and sludge-type wastes; however, Method 7471 is usually the method of choice for these waste types.) All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the liquid samples must be prepared according to the procedure discussed in this method.

2.2 Method 7470, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1.

4.9.1 The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system.

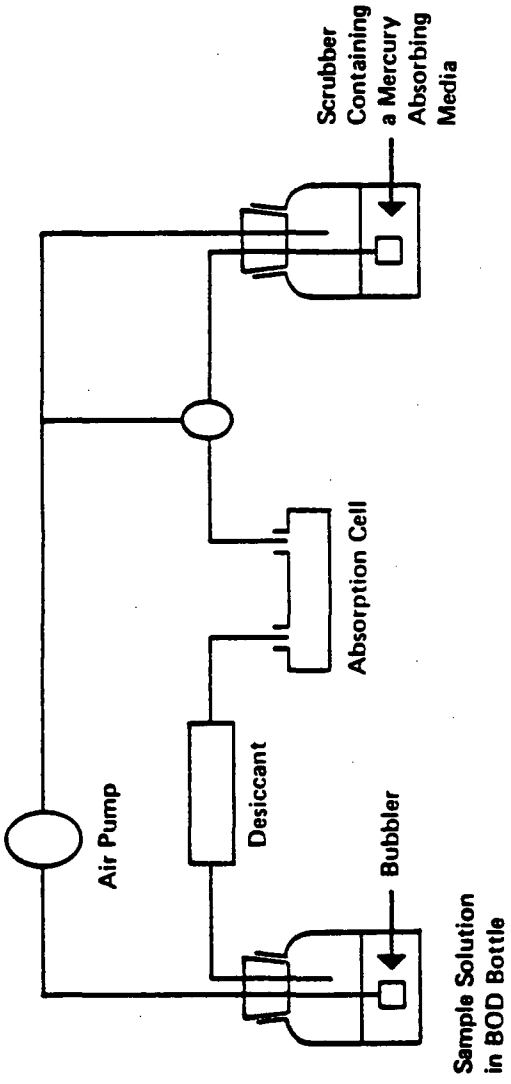


Figure 1. Apparatus for flameless mercury determination.

4.9.2 Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4; or
2. 0.25% Iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Sulfuric acid (H_2SO_4), concentrated: Reagent grade.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1.0 liter.

5.4 Nitric acid (HNO_3), concentrated: Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

5.5 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N H_2SO_4. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

5.6 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in Type II water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

5.7 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of Type II water.

5.8 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 mL of Type II water.

5.9 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of Type II water. Add 10 mL of concentrated HNO_3 and adjust the volume to 100.0 mL (1 mL = 1 mg Hg).

5.10 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 g per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before addition of the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH <2 with HNO_3. The suggested maximum holding times for these samples are 38 days in glass containers and 13 days in plastic containers.

6.4 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Transfer 100 mL, or an aliquot diluted to 100 mL, containing <1.0 g of mercury, to a 300-mL BOD bottle. Add 5 mL of H_2SO_4 and 2.5 mL of concentrated HNO_3, mixing after each addition. Add 15 mL of potassium permanganate solution to each sample bottle. Sewage samples may require additional permanganate. Ensure that equal amounts of permanganate are added to standards and blanks. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. After a delay of at least 30 sec, add 5 mL of stannous sulfate, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.2 Standard preparation: Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10.0-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles. Add enough Type II water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 to each bottle. Add 15 mL of $KMnO_4$ solution to each bottle and allow to stand at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized, wait 30 sec, add 5 mL of the stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.3 Analysis: At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter/min, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and

continue the aeration until the absorbance returns to its minimum valve. Close the bypass valve, remove the stopper and frit from the BOD bottle, and continue the aeration.

7.4 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

7.5 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions.

7.6 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.7 Calculate metal concentrations (1) by the method of standard additions, or (2) from a calibration curve. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

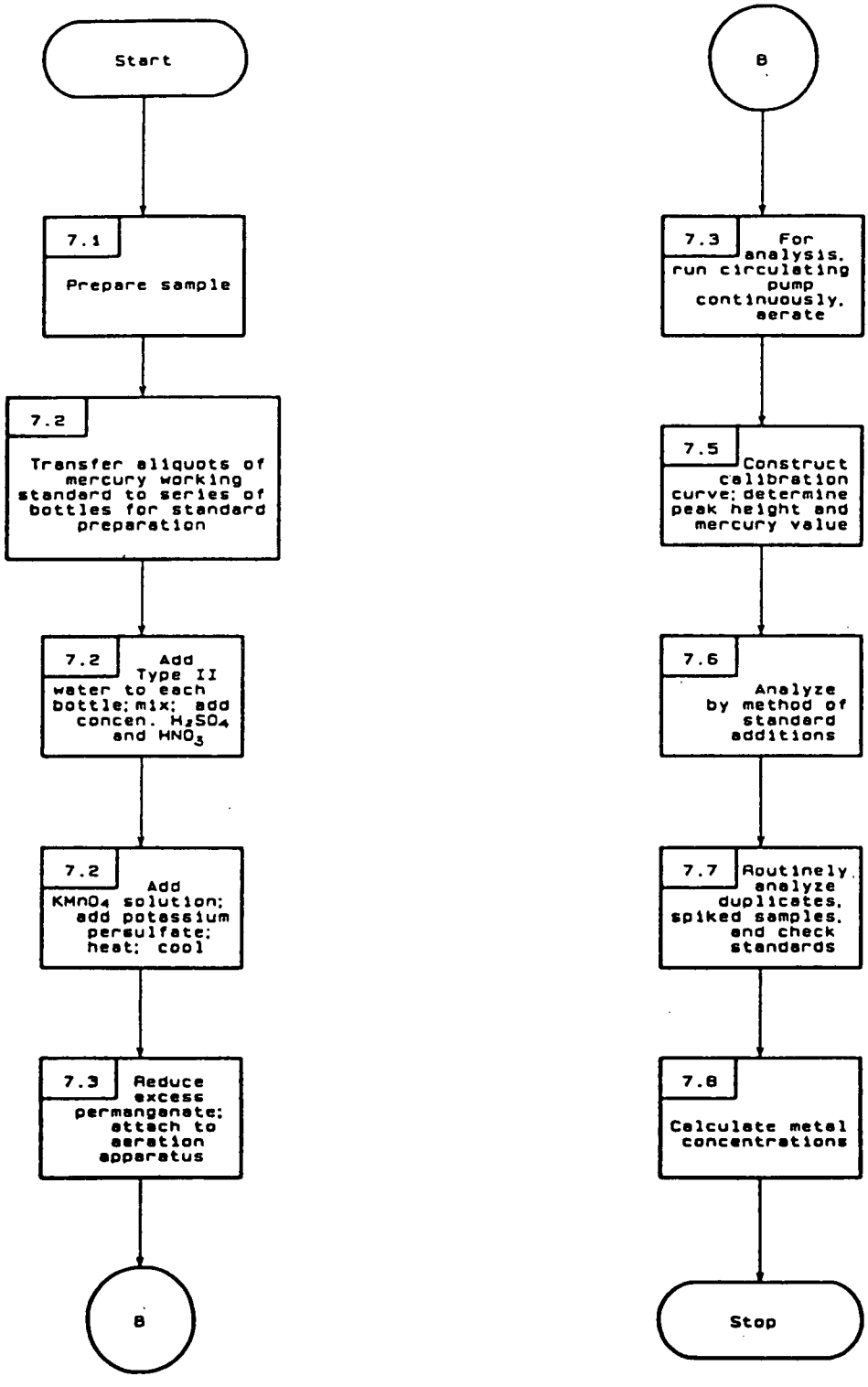
8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.1.


Start
7.1 Prepare sample
7.2 Transfer aliquots of mercury working standard to series of bottles for standard preparation
7.2 Add Type II water to each bottle; mix; add concen. H_2SO_4 and HNO_3
7.2 Add $KMnO_4$ solution; add potassium persulfate; heat; cool
7.3 Reduce excess permanganate; attach to aeration apparatus
B
B
7.3 For analysis, run circulating pump continuously, aerate
7.5 Construct calibration curve; determine peak height and mercury value
7.6 Analyze by method of standard additions
7.7 Routinely analyze duplicates, spiked samples, and check standards
7.8 Calculate metal concentrations
Stop

MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

2.2 Method 7471, a cold-vapor atomic absorption method, is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 L/min air may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 L/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1.

4.9.1 The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system.

4.9.2 Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the

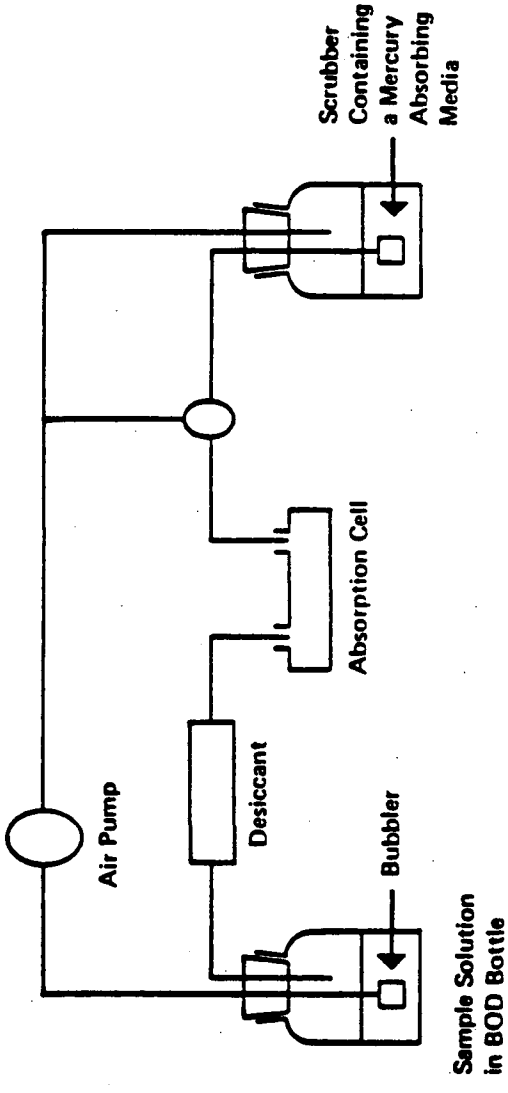


Figure 1. Apparatus for flameless mercury determination.

system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or
2. 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barneby and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1 liter.

5.4 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. A 10% solution of stannous chloride can be substituted for stannous sulfate.

5.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in Type II water and dilute to 100 mL. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

5.6 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of Type II water.

5.7 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of Type II water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg Hg).

5.8 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before adding the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH <2 with nitric acid.

6.4 For solids or semisolids, moisture may be driven off in a drying oven at a temperature of 60°C.

7.0 PROCEDURE

7.1 Sample preparation: Weigh triplicate 0.2-g portions of untreated sample and place in the bottom of a BOD bottle. Add 5 mL of Type II water and 5 mL of aqua regia. Heat 2 min in a water bath at 95°C. Cool; then add 50 mL Type II water and 15 mL potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

CAUTION: Do this addition under a hood, as Cl_2 could be evolved. Add 55 mL of Type II water. Treating each bottle individually, add 5 mL of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under step 7.4.

7.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 mL of concentrated H_2SO_4 and 2 mL of concentrated HNO_3 are added to the 0.2 g of sample. Add 5 mL of saturated $KMnO_4$ solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lb for 15 min. Cool, dilute to a volume of 100 mL with Type II water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under step 7.4.

7.3 Standard preparation: Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles. Add enough Type II water to each bottle to make a total volume of 10 mL. Add 5 mL of aqua regia and heat 2 min in a water bath at 95°C. Allow the sample to cool; add 50 mL Type II water and 15 mL of $KMnO_4$ solution to each bottle and return to the water bath for 30 min. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 mL of Type II water. Treating each bottle individually, add 5 mL of stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Step 7.4.

7.4 Analysis: At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 L/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle, and continue the aeration.

7.5 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

7.6 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions (see Method 7000, Section 8.7).

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.5 of Methods for Chemical Analysis of Water and Wastes.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

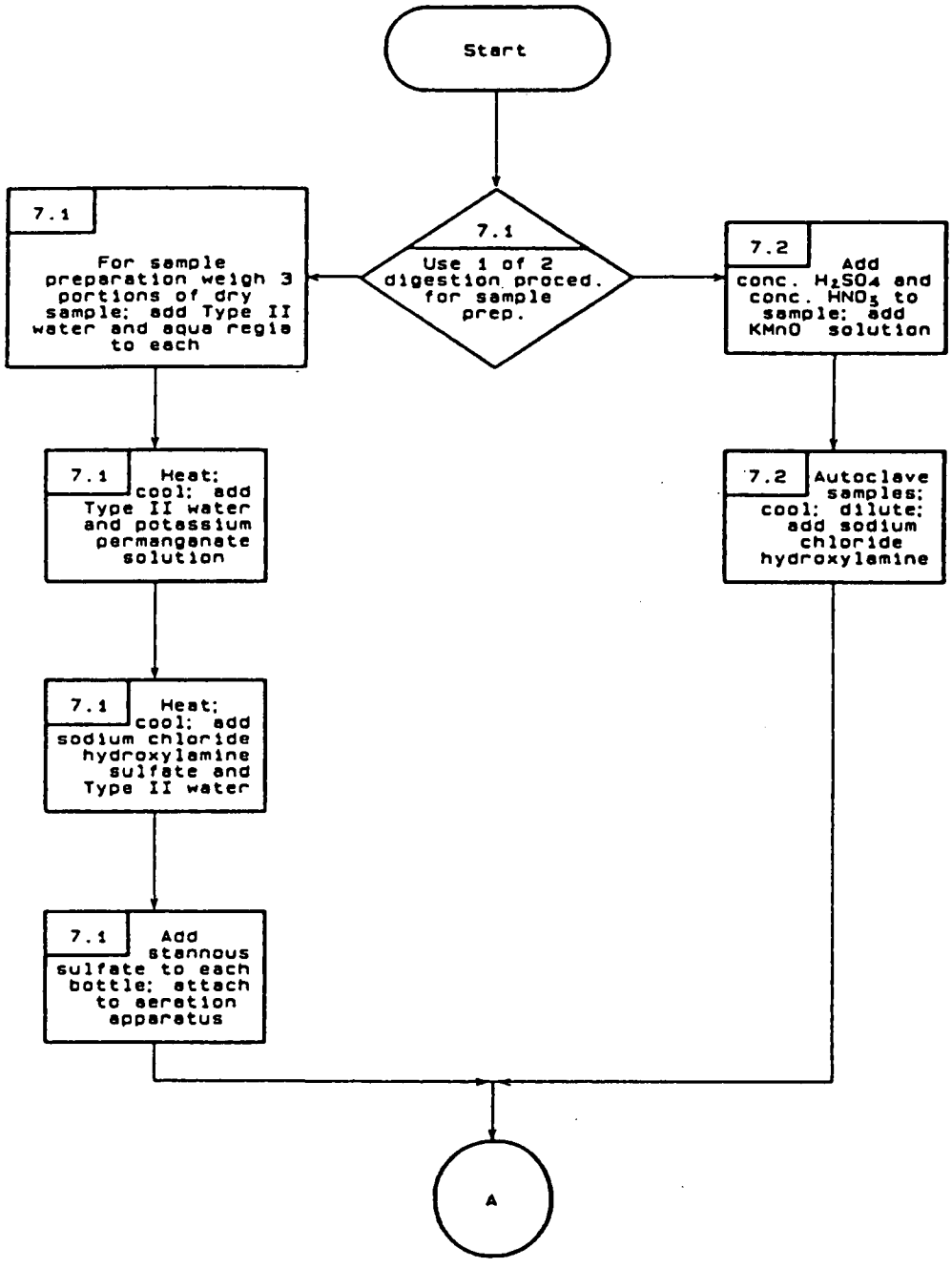
10.0 REFERENCES

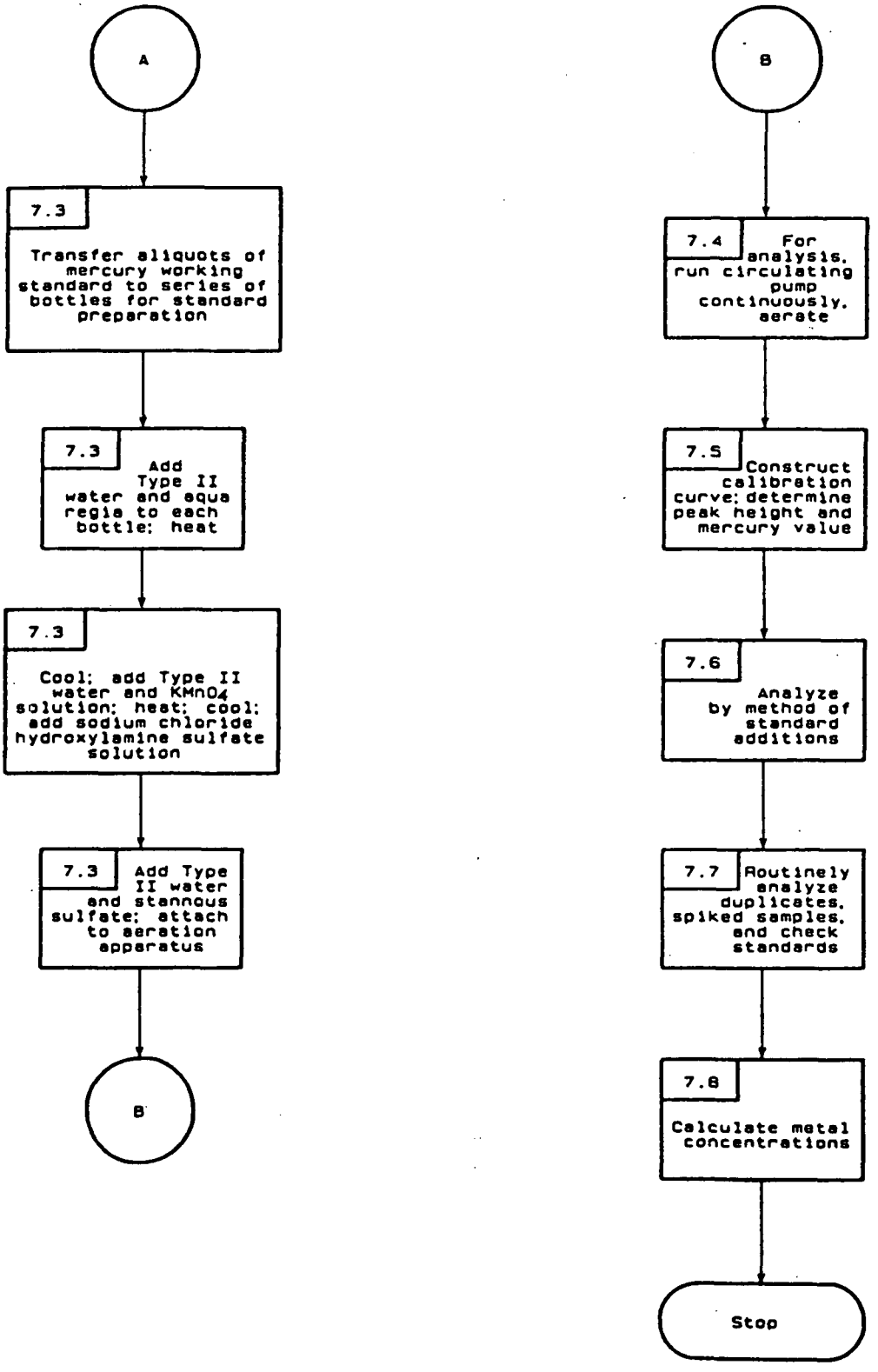
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.5.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	Not known	12, 12 ug/g
Wastewater treatment sludge	Not known	0.4, 0.28 ug/g


Start
7.1
Use 1 of 2 digestion proced. for sample prep.
7.1
For sample preparation weigh 3 portions of dry sample; add Type II water and aqua regia to each
7.2
Add conc. H_2SO_4 and conc. HNO_3 to sample; add KMnO solution
7.1
Heat; cool; add Type II water and potassium permanganate solution
7.2
Autoclave samples; cool; dilute; add sodium chloride hydroxylamine
7.1
Heat; cool; add sodium chloride hydroxylamine sulfate and Type II water
7.1
Add stannous sulfate to each bottle; attach to aeration apparatus
A


A
7.3
Transfer aliquots of mercury working standard to series of bottles for standard preparation
7.3
Add Type II water and aqua regia to each bottle; heat
7.3
Cool; add Type II water and KMnO4 solution; heat; cool; add sodium chloride hydroxylamine sulfate solution
7.3
Add Type II water and stannous sulfate; attach to aeration apparatus
B
B
7.4
For analysis, run circulating pump continuously, aerate
7.5
Construct calibration curve; determine peak height and mercury value
7.6
Analyze by method of standard additions
7.7
Routinely analyze duplicates, spiked samples, and check standards
7.8
Calculate metal concentrations
Stop

METHOD 7480

MOLYBDENUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Interferences in an air/acetylene flame from Ca, Sr, SO_4, and Fe are severe. These interferences are greatly reduced in the nitrous oxide flame and by addition of 1,000 mg/L aluminum to samples and standards.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Molybdenum hollow cathode lamp.**
4.2.2 **Wavelength:** 313.3 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Nitrous oxide.
4.2.5 **Type of flame:** Fuel rich.
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.840 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (analytical reagent grade), in Type II water and dilute to 1 liter; 1 mL = 1 mg Mo (1,000 mg/L). Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

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Date September 1986

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing. The samples and standards should also contain 1,000 mg/L aluminum (see Paragraph 5.2.3).

5.2.3 **Aluminum nitrate solution:** Dissolve 139 g aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$, in 150 mL of Type II water; heat to effect solution. Allow to cool and make up to 200 mL. To each 100 mL of standard and sample alike, add 2 mL of the aluminum nitrate solution.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

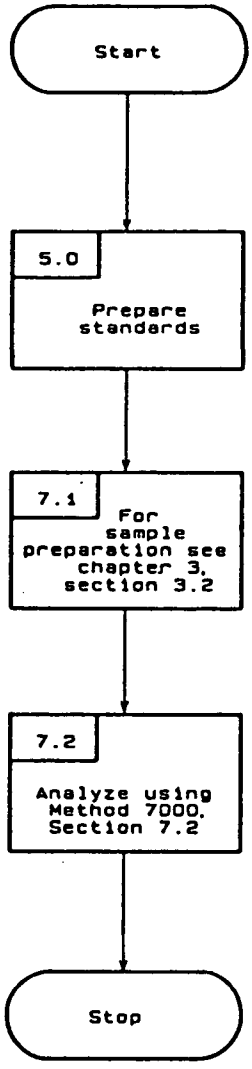
Optimum concentration range: 1-40 mg/L with a wavelength of 313.3 nm.
Sensitivity: 0.4 mg/L.
Detection limit: 0.1 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 0.3, 1.5, and 7.5 mg/L gave standard deviations of ±0.007, ±0.02, and ±0.07, respectively. Recoveries at these levels were 100%, 96%, and 95%, respectively.

9.3 For concentrations of molybdenum below 0.2 mg/L, the furnace technique (Method 7481) is recommended.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 246.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

MOLYBDENUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Molybdenum is prone to carbide formation. Use a pyrolytically coated graphite tube.

3.3 Memory effects are possible, and cleaning of the furnace may be required after analysis of more concentrated samples or standards.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Drying time and temp:** 30 sec at 125°C.
4.2.2 **Ashing time and temp:** 30 sec at 1400°C.
4.2.3 **Atomizing time and temp:** 5 sec at 2800°C.
4.2.4 **Purge gas:** Argon (nitrogen should not be used).
4.2.5 **Wavelength:** 313.3 nm.
4.2.6 **Background correction:** Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.
4.2.8 **Pyrolytically coated graphite tube.**

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.840 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (analytical reagent grade), in Type II water and dilute to 1 liter; 1 mL = 1 mg Mo (1,000 mg/L). Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

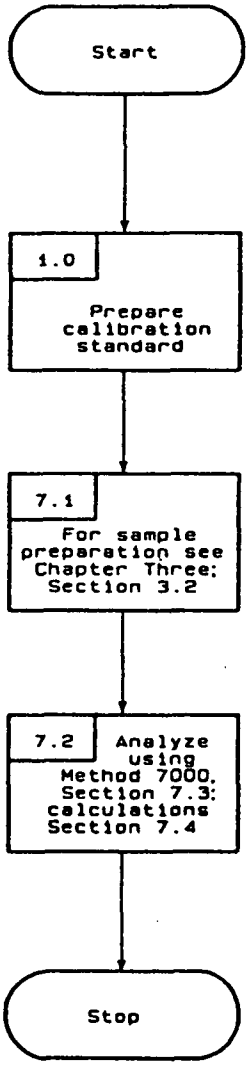
9.1 Precision and accuracy data are not available at this time.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 3-60 ug/L.
Detection limit: 1 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 246.2.


Start
1.0
Prepare calibration standard
7.1
For sample preparation see Chapter Three: Section 3.2
7.2
Analyze using Method 7000, Section 7.3: calculations Section 7.4
Stop

METHOD 7520

NICKEL (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction is required.

3.3 High concentrations of iron, cobalt, or chromium may interfere, requiring either matrix matching or use of a nitrous-oxide/acetylene flame.

3.4 A nonresonance line of Ni at 232.14 nm causes nonlinear calibration curves at moderate to high nickel concentrations, requiring sample dilution or use of the 352.4-nm line.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Nickel hollow cathode lamp.**
4.2.2 **Wavelength:** 232.0 nm (primary); 352.4 nm (alternate).
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Oxidizing (fuel lean).
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g nickel metal (analytical reagent grade) or 4.953 g nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$ (analytical reagent grade), in 10 mL HNO_3 and dilute to 1 liter with Type II water.

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Date September 1986

Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.3-5 mg/L with a wavelength of 232.0 nm.
Sensitivity: 0.15 mg/L.
Detection limit: 0.04 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 0.2, 1.0, and 5.0 mg/L gave standard deviations of ±0.011, ±0.02, and ±0.04, respectively. Recoveries at these levels were 100%, 97%, and 93%, respectively.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

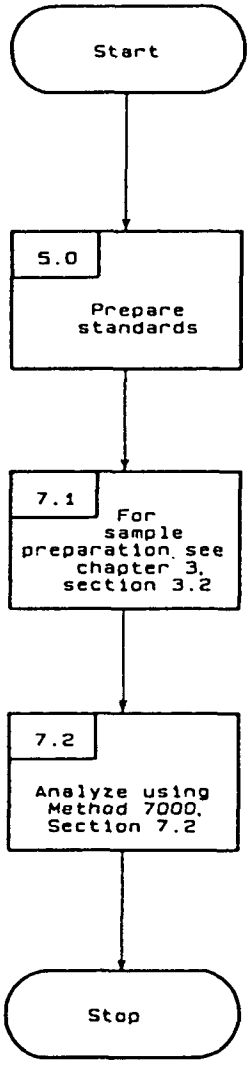
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 249.1

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	3050	13,000, 10,400 ug/g


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7550

OSMIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 Method 7550 is an atomic absorption procedure approved for determining the concentration of osmium in wastes, mobility procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7550, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to the acid digestion procedure discussed in this method. Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedure described in Method 3040 may be applicable. Due to the very volatile nature of some osmium compounds, the applicability of a method to a sample must be verified by means of spiked samples or standard reference materials, or both.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into a nitrous oxide/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the osmium concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.3 mg/L; typical sensitivity is 1 mg/L.

3.0 INTERFERENCES

3.1 Background correction is required because nonspecific absorption and light scattering can be significant at the analytical wavelength.

3.2 Due to the volatility of osmium, standards must be made on a daily basis, and the applicability of sample-preparation techniques must be verified for the sample matrices of interest.

3.3 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

3.4 Osmium and its compounds are extremely toxic; therefore, extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer: Single- or dual-channel, single- or double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Osmium hollow cathode lamp.

4.3 Strip-chart recorder (optional).

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid (HNO_3): Acid should be analyzed to determine levels of impurities. If a method blank using the acide is <MDL, the acid can be used.

5.3 Osmium standard stock solution (1,000 mg/L): Procure a certified aqueous standard from a supplier and verify by comparison with a second standard. If necessary, standards can be made from osmium compounds. However, due to the toxicity of these compounds, this approach is not advised.

5.4 Osmium working standards: Prepare dilution of the stock solution at the time of analysis. These standards should be prepared to contain 1% (v/v) HNO_3 and 1% (v/v) H_2SO_4.

5.5 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.6 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions by replacing the cylinder before the pressure has fallen to 50 psig.

5.7 Nitrous oxide: Cylinder suitable for instrumental analysis.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH <2 with HNO_3.

6.4 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Aqueous samples should be prepared according to the procedure described in Paragraph 7.2. Sludge-type samples should be prepared according to Method 3050; samples containing oils, greases, or waxes may be prepared according to Method 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples, relevant standard reference materials, or both.

7.2 Sample preparation of aqueous samples:

7.2.1 Transfer a representative 100-mL aliquot of the well-mixed sample to a Griffin beaker and add 1 mL of concentrated HNO_3.

7.2.2 Place the beaker on a steam bath or hot plate and warm for 15 min. Cool the beaker and, if necessary, filter or centrifuge to remove insoluble material.

7.2.3 Add 1 mL of concentrated H_2SO_4 and adjust the volume back to 100 mL. The sample is now ready for analysis.

7.3 The 290.0-nm wavelength line and background correction shall be employed.

7.4 A fuel-rich nitrous oxide/acetylene flame shall be used.

7.5 Follow the manufacturer's operating instructions for all other instrument parameters.

7.6 Either (1) run a series of osmium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances, or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.7 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions.

7.8 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.9 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

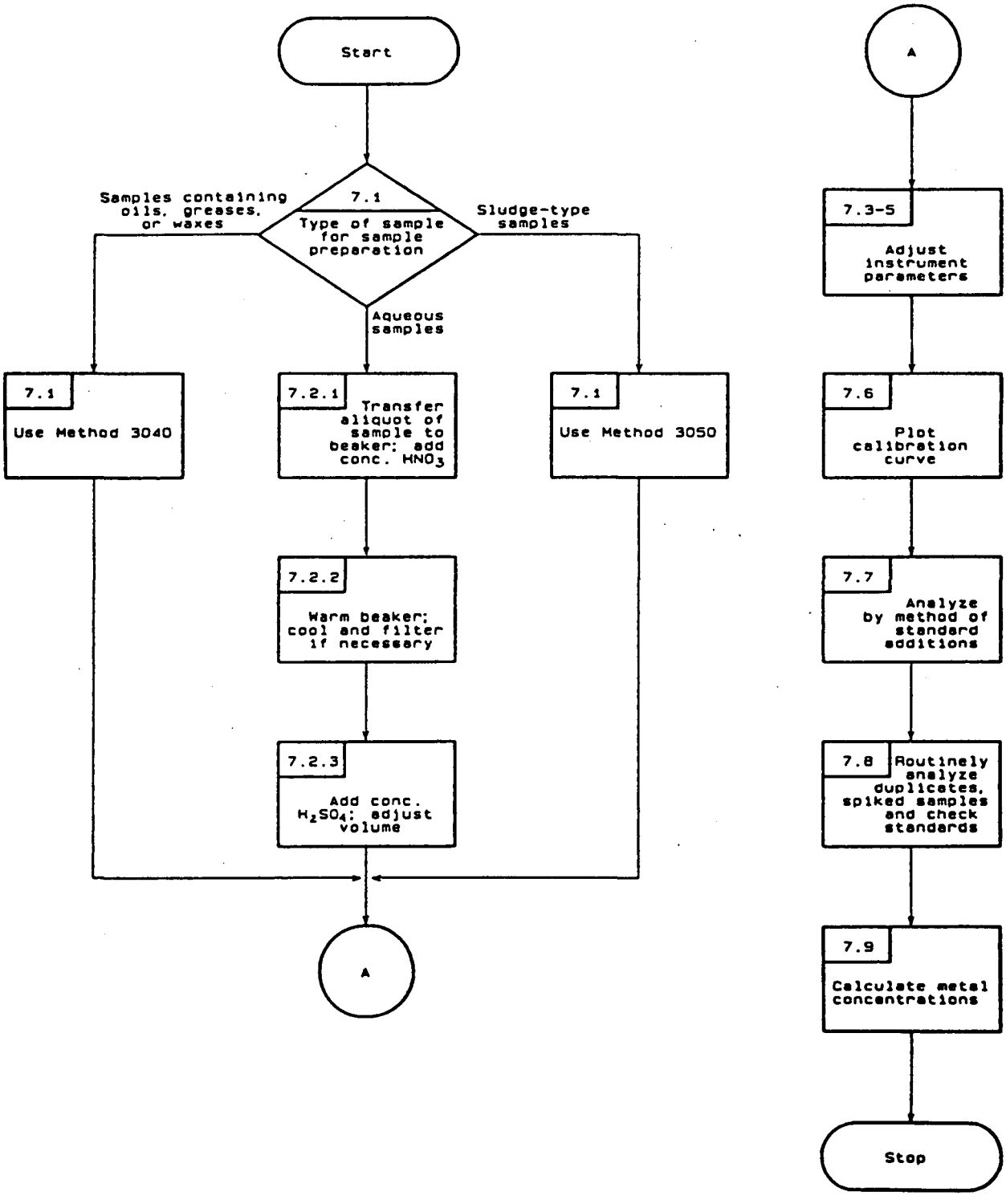
8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are not available at this time.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 252.1.


Start
7.1
Type of sample for sample preparation
Samples containing oils, greases, or waxes
Aqueous samples
Sludge-type samples
7.1
Use Method 3040
7.2.1
Transfer aliquot of sample to beaker; add conc. HNO3
7.1
Use Method 3050
7.2.2
Warm beaker; cool and filter if necessary
7.2.3
Add conc. H2SO4; adjust volume
A
A
7.3-5
Adjust instrument parameters
7.6
Plot calibration curve
7.7
Analyze by method of standard additions
7.8
Routinely analyze duplicates, spiked samples and check standards
7.9
Calculate metal concentrations
Stop

METHOD 7610

POTASSIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 In air/acetylene or other high-temperature flames (>2800°C), potassium can experience partial ionization, which indirectly affects absorption sensitivity. The presence of other alkali salts in the sample can reduce this ionization and thereby enhance analytical results. The ionization-suppressive effect of sodium is small if the ratio of Na to K is under 10. Any enhancement due to sodium can be stabilized by adding excess sodium (1,000 ug/mL) to both sample and standard solutions. If more stringent control of ionization is required, the addition of cesium should be considered. Reagent blanks should be analyzed to correct for potassium impurities in the buffer stock.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Potassium hollow cathode lamp.**
4.2.2 **Wavelength:** 766.5 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Slightly oxidizing (fuel lean).
4.2.6 **Background correction:** Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.907 g of potassium chloride, KCl (analytical reagent grade), dried at 110°C in Type II water and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

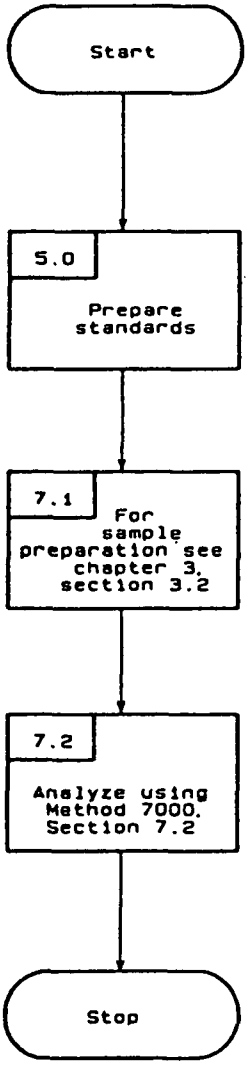
9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.1-2 mg/L with a wavelength of 766.5 nm.
Sensitivity: 0.04 mg/L.
Detection limit: 0.01 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 1.6 and 6.3 mg/L gave standard deviations of $\pm$0.2 and $\pm$0.5, respectively. Recoveries at these levels were 103% and 102%, respectively.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 258.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7740

SELENIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7740 is an atomic absorption procedure approved for determining the concentration of selenium in wastes, mobility-procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7740, samples must be prepared in order to convert organic forms of selenium to inorganic forms, to minimize organic interferences, and to convert samples to suitable solutions for analysis. The sample-preparation procedure varies, depending on the sample matrix. Aqueous samples are subjected to the acid-digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of lamp radiation during atomization will be proportional to the selenium concentration.

2.3 The typical detection limit for this method is 2 ug/L.

3.0 INTERFERENCES

3.1 Elemental selenium and many of its compounds are volatile; therefore, samples may be subject to losses of selenium during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A nickel nitrate solution must be added to all digestates prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, selenium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Selenium analysis is particularly susceptible to these problems because of its low analytical wavelength (196.0 nm). Simultaneous background correction is required to avoid erroneously high results. High iron levels can give overcorrection with deuterium background. Zeeman background correction can be useful in this situation.

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

3.5 Selenium analysis suffers interference from chlorides (>800 mg/L) and sulfate (>200 mg/L). The addition of nickel nitrate such that the final concentration is 1% nickel will lessen this interference.

4.0 APPARATUS AND MATERIALS

4.1 250-mL Griffin beaker.

4.2 10-mL volumetric flasks.

4.3 Atomic absorption spectrophotometer: Single- or dual-channel, single- or double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-800 nm, and provisions for simultaneous background correction and interfacing with a strip-chart recorder.

4.4 Selenium hollow cathode lamp, or electrodeless discharge lamp (EDL): EDLs provide better sensitivity for the analysis of Se.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Strip-chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis, such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1,000 uL, as required.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid (HNO_3): Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.3. Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If a method blank made with the oxidant is <MDL, the oxidant can be used.

5.4 Selenium standard stock solution (1,000 mg/L): Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 0.3453 g of selenious acid (actual assay 94.6% H_2SeO_3, analytical reagent grade) or equivalent in Type II water and dilute to 200 mL.

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ or equivalent in Type II water and dilute to 100 mL.

5.6 Nickel nitrate solution (1%): Dilute 20 mL of the 5% nickel nitrate to 100 mL with Type II water.

5.7 Selenium working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add 1 mL of concentrated HNO_3, 2 mL of 30% H_2O_2, and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with Type II water.

5.8 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.9 Hydrogen: Suitable for instrumental analysis.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Steps 7.1.1 to 7.1.3. Sludge-type samples should be prepared according to Method 3050. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer 100 mL of well-mixed sample to a 250-mL Griffin beaker; add 2 mL of 30% H_2O_2 and sufficient concentrated HNO_3 to result in an acid concentration of 1% (v/v). Heat for 1 hr at 95°C or until the volume is slightly less than 50 mL.

7.1.2 Cool and bring back to 50 mL with Type II water.

7.1.3 Pipet 5 mL of this digested solution into a 10-mL volumetric flask, add 1 mL of the 1% nickel nitrate solution, and dilute to 10 mL with Type II water. The sample is now ready for injection into the furnace.

7.2 The 196.0-nm wavelength line and a background correction system must be employed. Follow the manufacturer's suggestions for all other spectrophotometer parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured uL-aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.5 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions.

7.6 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.7 Duplicates, spiked samples, and check standards should be analyzed every 20 samples.

7.8 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 270.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

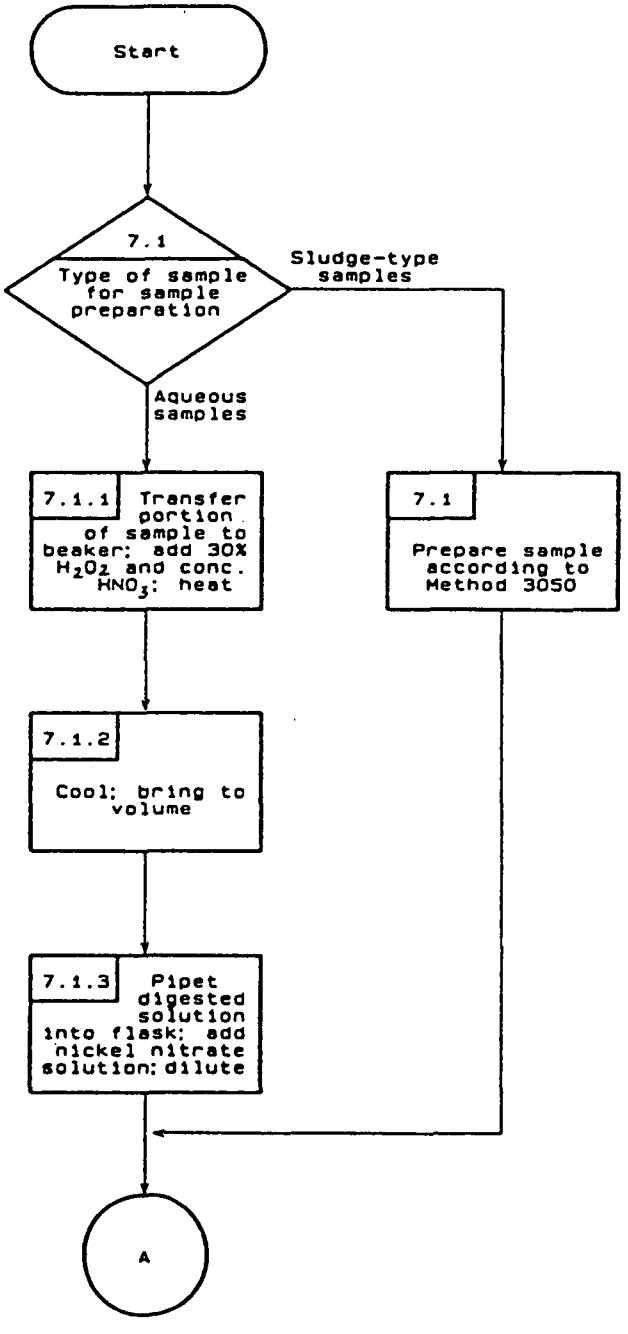
10.0 REFERENCES

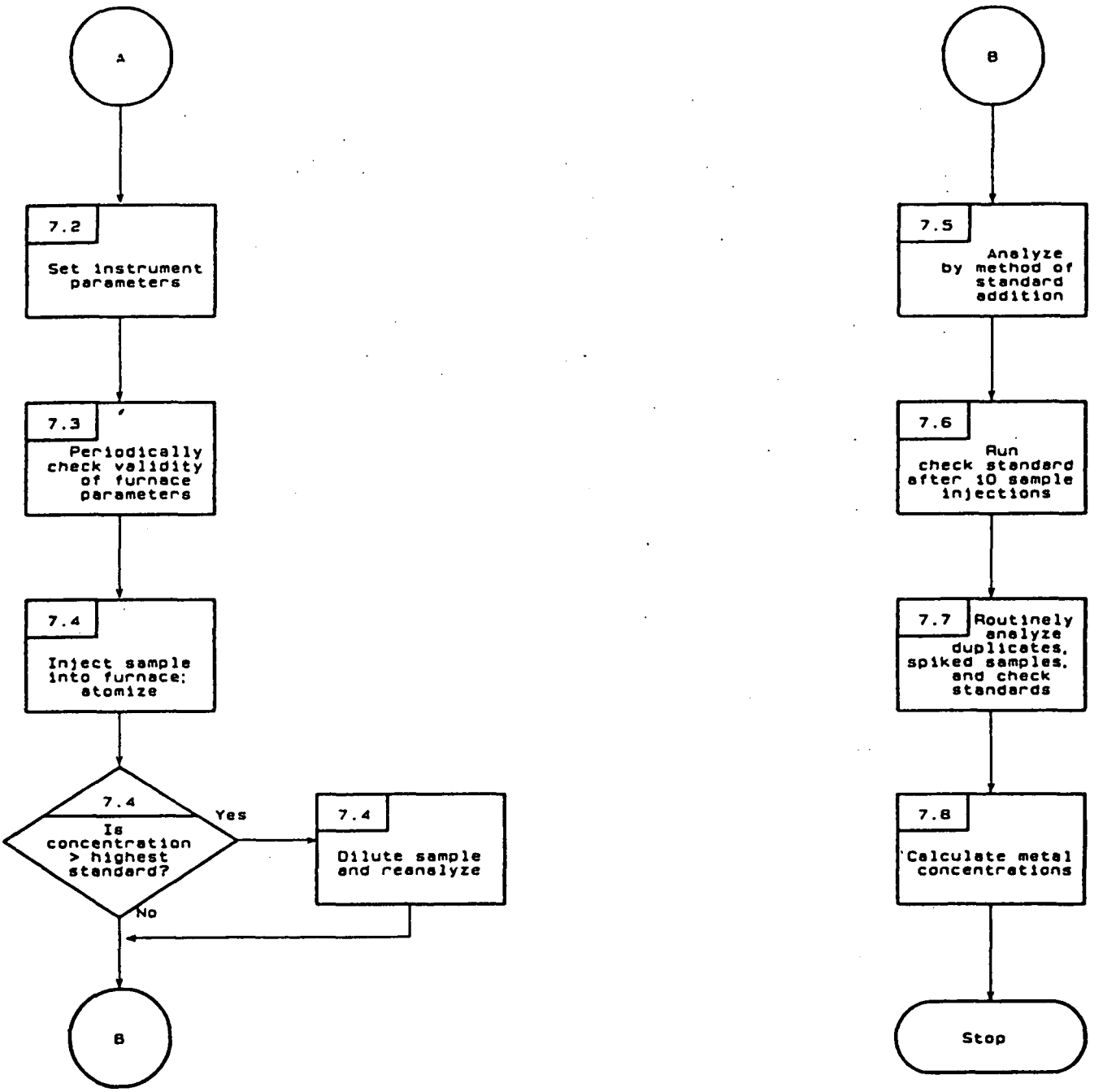
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 270.2.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	3050	14, 11 ug/g


Start
7.1
Type of sample for sample preparation
Sludge-type samples
Aqueous samples
7.1.1 Transfer portion of sample to beaker; add 30% H_2O_2 and conc. HNO_3; heat
7.1
Prepare sample according to Method 3050
7.1.2
Cool; bring to volume
7.1.3 Pipet digested solution into flask; add nickel nitrate solution; dilute
A


A
7.2
Set instrument parameters
7.3
Periodically check validity of furnace parameters
7.4
Inject sample into furnace; atomize
7.4
Is concentration > highest standard?
Yes
No
7.4
Dilute sample and reanalyze
B
B
7.5
Analyze by method of standard addition
7.6
Run check standard after 10 sample injections
7.7
Routinely analyze duplicates, spiked samples, and check standards
7.8
Calculate metal concentrations
Stop

METHOD 7741

SELENIUM (ATOMIC ABSORPTION, GASEOUS HYDRIDE)

1.0 SCOPE AND APPLICATION

1.1 Method 7741 is an atomic absorption procedure that is approved for determining the concentration of selenium in wastes, mobility-procedure extracts, soils, and ground water, provided that the sample matrix does not contain high concentrations of chromium, copper, mercury, silver, cobalt, or molybdenum. All samples must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are employed to determine applicability of the method to a given waste.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric/sulfuric acid digestion procedure described in this method. Next, the selenium in the digestate is reduced to Se(IV) with tin chloride. The Se(IV) is then converted to a volatile hydride with hydrogen produced from a zinc/HCl reaction.

2.2 The volatile hydride is swept into an argon-hydrogen flame located in the optical path of an atomic absorption spectrophotometer; the resulting absorbance is proportional to the selenium concentration.

2.3 The typical detection limit for this method is 0.002 mg/L.

3.0 INTERFERENCES

3.1 High concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver can cause analytical interferences.

3.2 Traces of nitric acid left following the sample work-up can result in analytical interferences. Nitric acid must be distilled off the sample by heating the sample until fumes of SO_3 are observed.

3.3 Elemental selenium and many of its compounds are volatile; therefore, certain samples may be subject to losses of selenium during sample preparation.

4.0 APPARATUS AND MATERIALS

4.1 100-mL beaker.

4.2 Electric hot plate.

4.3 A commercially available zinc slurry hydride generator or a generator constructed from the following material (see Figure 1):

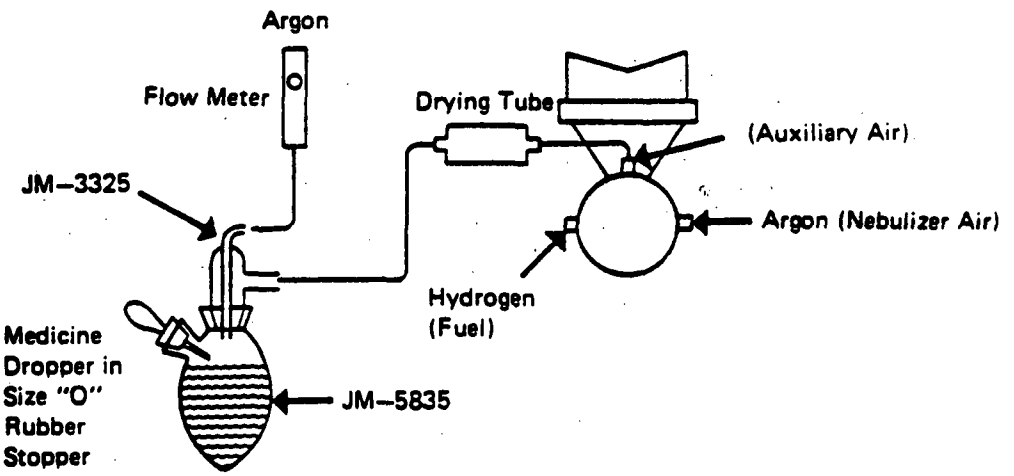


Figure 1. Zinc slurry hydride generator apparatus set-up and AAS sample introduction system.

4.3.1 **Medicine dropper:** Fitted into a size "0" rubber stopper capable of delivering 1.5 mL.

4.3.2 **Reaction flask:** 50-mL, pear-shaped, with two 14/20 necks (Scientific Glass, JM-5835).

4.3.3 **Gas inlet-outlet tube:** Constructed from a micro cold-finger condenser (JM-3325) by cutting the portion below the 14/20 ground-glass joint.

4.3.4 **Magnetic stirrer:** To homogenize the zinc slurry.

4.3.5 **Polyethylene drying tube:** 10-cm, filled with glass to prevent particulate matter from entering the burner.

4.3.6 **Flow meter:** Capable of measuring 1 liter/min.

4.4 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-800 nm, and provisions for interfacing with a strip-chart recorder and simultaneous background correction.

4.5 Burner: Recommended by the particular instrument manufacturer for the argon-hydrogen flame.

4.6 Selenium hollow cathode lamp or electrodeless discharge lamp.

4.7 Strip-chart recorder (optional).

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.3 Concentrated sulfuric acid: Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.4 Concentrated hydrochloric acid: Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.5 Diluent: Add 100 mL 18 N H_2SO_4 and 400 mL concentrated HCl to 400 mL Type II water and dilute to a final volume of 1 liter with Type II water.

5.6 Potassium iodide solution: Dissolve 20 g KI in 100 mL Type II water.

5.7 Stannous chloride solution: Dissolve 100 g $SnCl_2$ in 100 mL of concentrated HCl.

5.8 Selenium standard stock solution: 1,000 mg/L solution may be purchased, or prepared as follows: Dissolve 0.3453 g of selenious acid (assay 94.6% of H_2SeO_3) in Type II water. Add to a 200-mL volumetric flask and bring to volume (1 mL = 1 mg Se).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation:

7.1.1 To a 50-mL aliquot of digested sample (or, in the case of EP extracts, a 50-mL sample) add 10 mL of concentrated HNO_3 and 12 mL of 18 N H_2SO_4. Evaporate the sample on a hot plate until white SO_3 fumes are observed (a volume of about 20 mL). Do not let it char. If it chars, stop the digestion, cool, and add additional HNO_3. Maintain an excess of HNO_3 (evidence of brown fumes) and do not let the solution darken because selenium may be reduced and lost. When the sample remains colorless or straw yellow during evolution of SO_3 fumes, the digestion is complete.

7.1.2 Cool the sample, add about 25 mL Type II water, and again evaporate to SO_3 fumes just to expel oxides of nitrogen. Cool. Add 40 mL concentrated HCl and bring to a volume of 100 mL with Type II water.

7.2 Prepare working standards from the standard stock solutions. The following procedures provide standards in the optimum range.

7.2.1 To prepare a **working stock solution**, pipet 1 mL standard stock solution (see Paragraph 5.8) into a 1-liter volumetric flask. Bring to volume with Type II water containing 1.5 mL concentrated HNO_3/liter. The concentration of this solution is 1 mg Se/L (1 mL = 1 ug Se).

7.2.2 Prepare six **working standards** by transferring 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of the working stock solution (see Paragraph 7.2.1) into 100-mL volumetric flasks. Bring to volume with diluent. The concentrations of these working standards are 0, 5, 10, 15, 20, and 25 ug Se/L.

7.3 Standard additions:

7.3.1 Take the 15-, 20-, and 25-ug standards and transfer quantitatively 25 mL from each into separate 50-mL volumetric flasks. Add 10 mL of the prepared sample to each. Bring to volume with Type II water containing 1.5 mL HNO_3/liter.

7.3.2 Add 10 mL of prepared sample to a 50-mL volumetric flask. Bring to volume with Type II water containing 1.5 mL HNO_3/liter. This is the blank.

7.4 Follow the manufacturer's instructions for operating an argon-hydrogen flame. The argon-hydrogen flame is colorless; therefore, it may be useful to aspirate a low concentration of sodium to ensure that ignition has occurred.

7.5 The 196.0-nm wavelength shall be used for the analysis of selenium.

7.6 Transfer a 25-mL portion of the digested sample or standard to the reaction vessel. Add 0.5 mL $SnCl_2$ solution. Allow at least 10 min for the metal to be reduced to its lowest oxidation state. Attach the reaction vessel to the special gas inlet-outlet glassware. Fill the medicine dropper with 1.50 mL zinc slurry that has been kept in suspension with the magnetic stirrer. Firmly insert the stopper containing the medicine dropper into the side neck of the reaction vessel. Squeeze the bulb to introduce the zinc slurry into the sample or standard solution. The metal hydride will produce a peak almost immediately. When the recorder pen returns partway to the base line, remove the reaction vessel.

7.7 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions.

7.8 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.9 Calculate metal concentrations: (1) by the method of standard additions (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken

into account. For example, if the method of standard additions was employed, the analytical value will be one-tenth the concentration of the original sample due to dilution during preparation.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

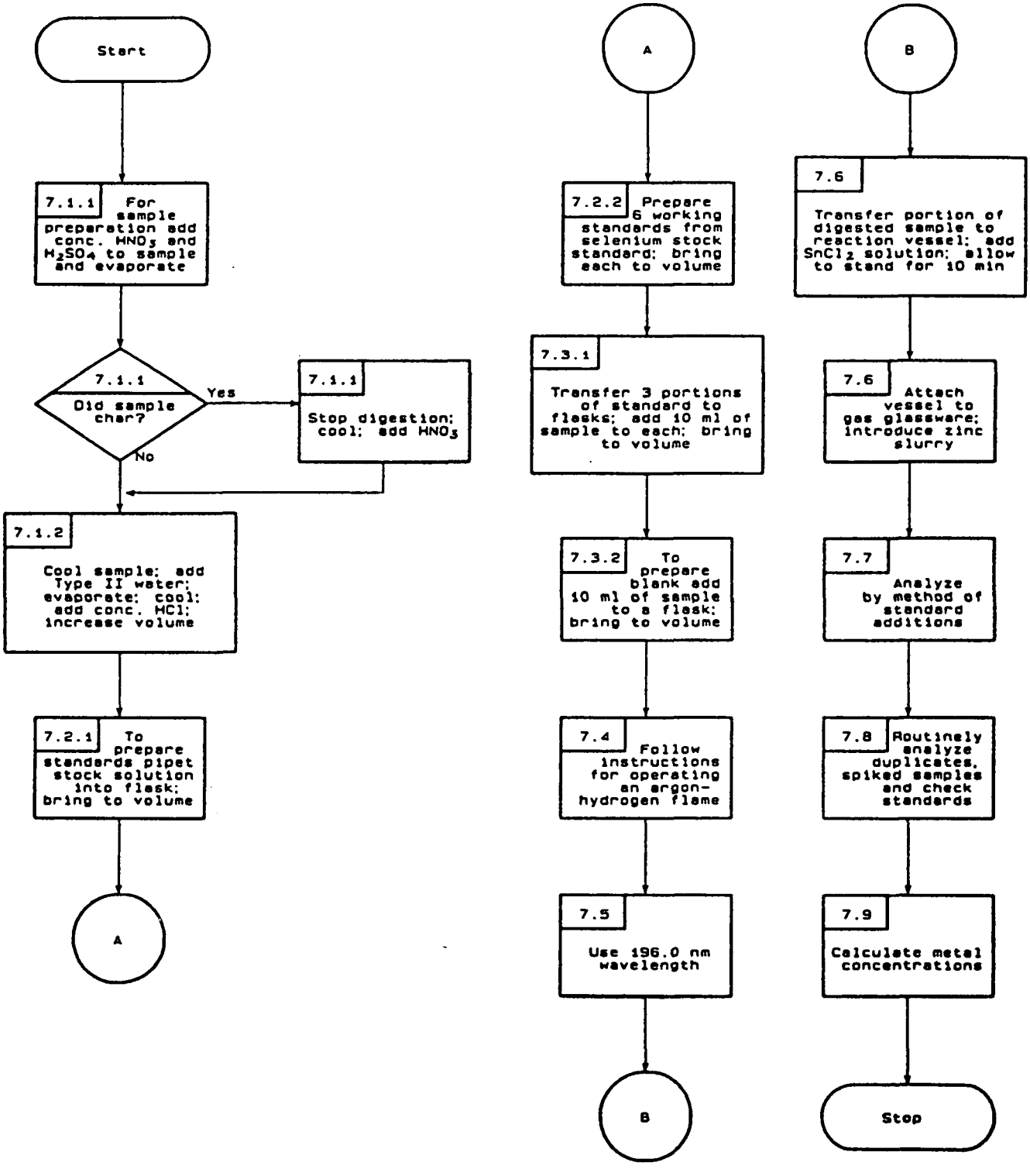
8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 270.3 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 270.3.


Start
7.1.1 For sample preparation add conc. HNO_3 and H_2SO_4 to sample and evaporate
7.1.1 Did sample char?
Yes
No
7.1.1 Stop digestion; cool; add HNO_3
7.1.2 Cool sample; add Type II water; evaporate; cool; add conc. HCl; increase volume
7.2.1 To prepare standards pipet stock solution into flask; bring to volume
A
A
7.2.2 Prepare 6 working standards from selenium stock standard; bring each to volume
7.3.1 Transfer 3 portions of standard to flasks; add 10 ml of sample to each; bring to volume
7.3.2 To prepare blank add 10 ml of sample to a flask; bring to volume
7.4 Follow instructions for operating an argon-hydrogen flame
7.5 Use 196.0 nm wavelength
B
B
7.6 Transfer portion of digested sample to reaction vessel; add $SnCl_2$ solution; allow to stand for 10 min
7.6 Attach vessel to gas glassware; introduce zinc slurry
7.7 Analyze by method of standard additions
7.8 Routinely analyze duplicates, spiked samples and check standards
7.9 Calculate metal concentrations
Stop

METHOD 7760

SILVER (ATOMIC ABSORPTION, DIRECT ASPIRATON)

1.0 SCOPE AND APPLICATION

1.1 Method 7760 is an atomic absorption procedure approved for determining the concentration of silver in wastes, mobility procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7760, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to the acid-digestion procedure described in this method.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the silver concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.01 mg/L; typical sensitivity is 0.06 mg/L.

3.0 INTERFERENCES

3.1 Background correction is required because nonspecific absorption and light scattering may occur at the analytical wavelength.

3.2 Silver nitrate solutions are light-sensitive and have the tendency to plate out on container walls. Thus silver standards should be stored in brown bottles.

3.3 Silver chloride is insoluble; therefore, hydrochloric acid should be avoided unless the silver is already in solution as a chloride complex.

3.4 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer: Single- or dual-channel, single- or double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Silver hollow cathode lamp.

4.3 Strip-chart recorder (optional).

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid (HNO_3): Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Concentrated ammonium hydroxide (NH_4OH): Base should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.4 Silver standard stock solution (1,000 mg/L): Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 0.7874 g anhydrous silver nitrate ($AgNO_3$), analytical reagent grade, in Type II water. Add 5 mL concentrated HNO_3 and bring to volume in a 500-mL volumetric flask (1 mL = 1 mg Ag).

5.5 Silver working standards: These standards should be prepared with nitric acid and at the same concentrations as the analytical solution.

5.6 Iodine solution, 1 N: Dissolve 20 g potassium iodide (KI), analytical reagent grade, in 50 mL Type II water. Add 12.7 g iodine (I_2), analytical reagent grade, and dilute to 100 mL. Place in a brown bottle.

5.7 Cyanogen iodide solution: To 50 mL Type II water add 4.0 mL concentrated NH_4OH, 6.5 g KCN, and 5.0 mL of iodine solution. Mix and dilute to 100 mL with Type II water. Do not keep longer than 2 wk.

CAUTION: This reagent cannot be mixed with any acid solutions because toxic hydrogen cyanide will be produced.

5.8 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.9 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions by replacing the cylinder before the pressure has fallen to 50 psig.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH <2 with nitric acid.

6.4 When possible, standards and samples should be stored in the dark and in brown bottles.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Aqueous samples should be prepared according to Paragraphs 7.2 and 7.3. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 Preparation of aqueous samples:

7.2.1 Transfer a representative aliquot of the well-mixed sample to a Griffin beaker and add 3 mL of concentrated HNO_3. Cover the beaker with a watch glass. Place the beaker on a hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. DO NOT BAKE. Cool the beaker and add another 3-mL portion of concentrated HNO_3. Re-cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If the sample contains thiosulfates, this step may result in splatter of sample out of the beaker as the sample approaches dryness. This has been reported to occur with certain photographic types of samples.

7.2.2 Continue heating, adding additional acid, as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of HNO_3 so that the final dilution contains 0.5% (v/v) HNO_3 and warm the beaker to dissolve any precipitate or residue resulting from evaporation.

7.2.3 Wash down the beaker walls and watch glass with Type II water and, when necessary, filter the sample to remove silicates and other insoluble material that could clog the nebulizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis.

7.3 If plating out of AgCl is suspected, the precipitate can be redissolved by adding cyanogen iodide to the sample.

CAUTION: This can be done only after digestion to prevent formation of toxic cyanide under acid conditions.

If cyanogen iodide addition to the sample is necessary, then the standards must be treated in the same manner.

CAUTION: Cyanogen iodide must not be added to the acidified silver standards.

New standards must be made, as directed in Paragraphs 5.4 and 5.5, except that the acid addition step must be omitted. Transfer 10 mL of stock solution to a small beaker. Add Type II water to make about 80 mL. Make the solution basic (pH above 7) with ammonium hydroxide. Rinse the pH meter electrodes into the solution with Type II water. Add 1 mL cyanogen iodide and allow to stand 1 hr. Transfer quantitatively to a 100-mL volumetric flask and bring to volume with Type II water.

7.4 The 328.1-nm wavelength line and background correction shall be employed.

7.5 An oxidizing air-acetylene flame shall be used.

7.6 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.7 Either (1) run a series of silver standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances, or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.8 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions.

7.9 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.10 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 272.1 of Methods for Chemical Analysis of Water and Wastes.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

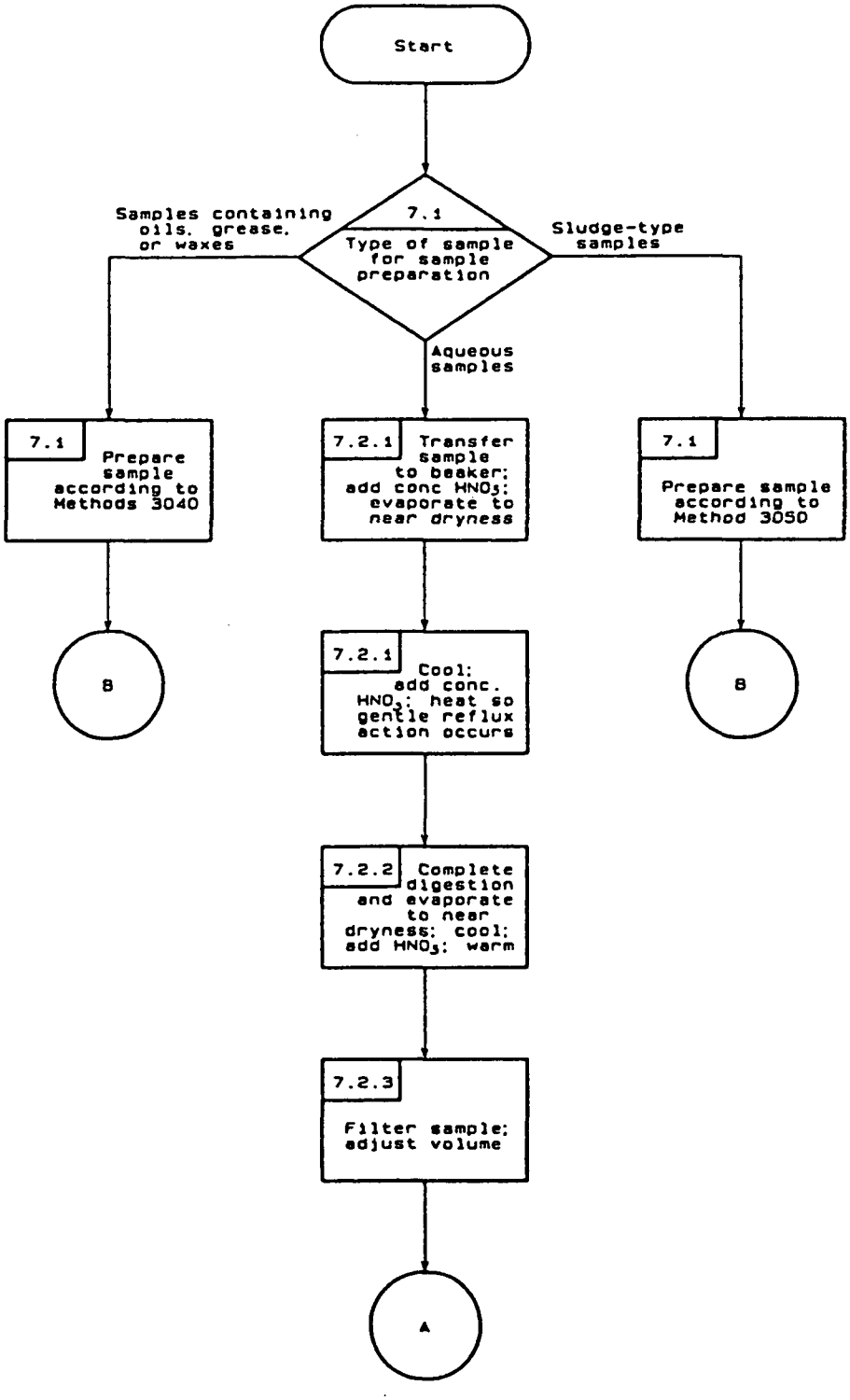
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 272.1.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	3050	2.3, 1.6 ug/g
Emission control dust	3050	1.8, 4.2 ug/g



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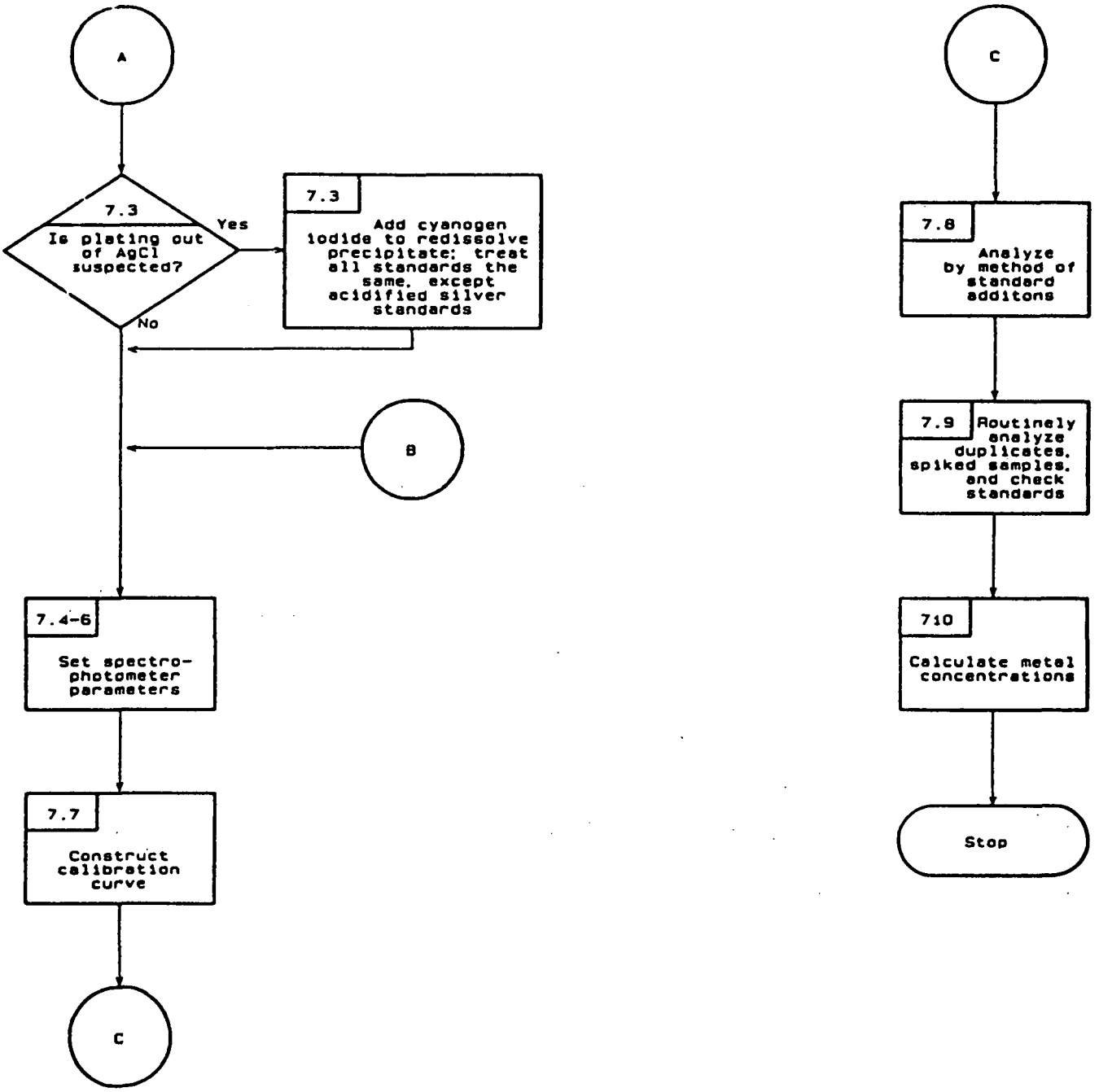

A
7.3
Is plating out of AgCl suspected?
Yes
No
7.3
Add cyanogen iodide to redissolve precipitate; treat all standards the same, except acidified silver standards
B
7.4-6
Set spectro-photometer parameters
7.7
Construct calibration curve
C
C
7.8
Analyze by method of standard additons
7.9
Routinely analyze duplicates, spiked samples, and check standards
710
Calculate metal concentrations
Stop

METHOD 7770

SODIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Ionization interferences can affect analysis for sodium; therefore, samples and standards must be matrix matched or an ionization suppressant employed.

3.3 Sodium is a universal contaminant, and great care should be taken to avoid contamination.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Sodium hollow cathode lamp.**
4.2.2 **Wavelength:** 589.6 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Oxidizing (fuel lean).
4.2.6 **Background correction:** Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 2.542 g sodium chloride, NaCl (analytical reagent grade), in Type II water, acidify with 10 mL redistilled HNO_3, and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

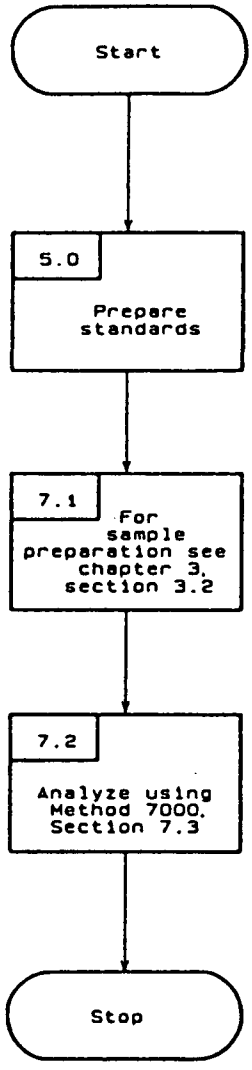
9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.03-1 mg/L with a wavelength of 589.6 nm.
Sensitivity: 0.015 mg/L.
Detection limit: 0.002 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 8.2 and 52 mg/L gave standard deviations of $\pm$0.1 and $\pm$0.8, respectively. Recoveries at these levels were 102% and 100%, respectively.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 273.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.3
Stop

METHOD 7840

THALLIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction is required.

3.3 Hydrochloric acid should not be used.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Thallium hollow cathode lamp.**
4.2.2 **Wavelength:** 276.8 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Oxidizing (fuel lean).
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.303 g thallium nitrate, $TlNO_3$ (analytical reagent grade), in Type II water, acidify with 10 mL concentrated HNO_3, and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

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5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

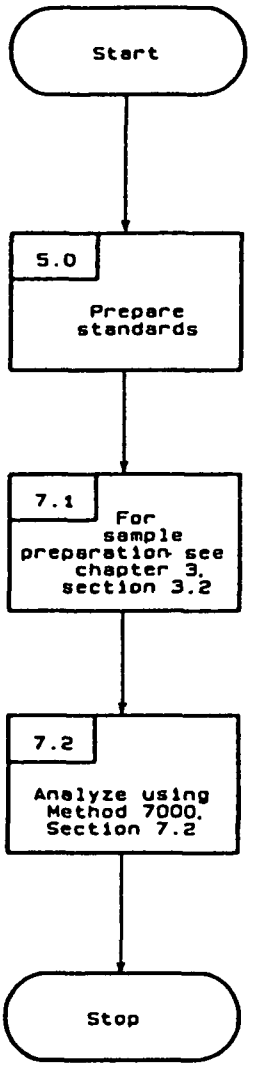
Optimum concentration range: 1-20 mg/L with a wavelength of 276.8 nm.
Sensitivity: 0.5 mg/L.
Detection limit: 0.1 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 0.6, 3, and 15 mg/L gave standard deviations of ±0.018, ±0.05, and ±0.2, respectively. Recoveries at these levels were 100%, 98%, and 98%, respectively.

9.3 For concentrations of thallium below 0.2 mg/L, the furnace technique (Method 7841) is recommended.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 279.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

THALLIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction is required.

3.3 Hydrochloric acid or excessive chloride will cause volatilization of thallium at low temperatures. Verification that losses are not occurring, by spiked samples or standard additions, must be made for each sample matrix.

3.4 Palladium is a suitable matrix modifier for thallium analysis.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Drying time and temp:** 30 sec at 125°C.
4.2.2 **Ashing time and temp:** 30 sec at 400°C.
4.2.3 **Atomizing time and temp:** 10 sec at 2400°C.
4.2.4 **Purge gas:** Argon or nitrogen.
4.2.5 **Wavelength:** 276.8 nm.
4.2.6 **Background correction:** Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

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5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.303 g thallium nitrate, $TlNO_3$ (analytical reagent grade), in Type II water, acidify with 10 mL concentrated HNO_3, and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing (0.5% v/v HNO_3).

5.3 Palladium chloride: Weigh 0.25 g of $PdCl_2$ to the nearest 0.0001 g. Dissolve in 10 mL of 1:1 HNO_3 and dilute to 1 liter with Type II water. Use equal volumes of sample and palladium solution.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

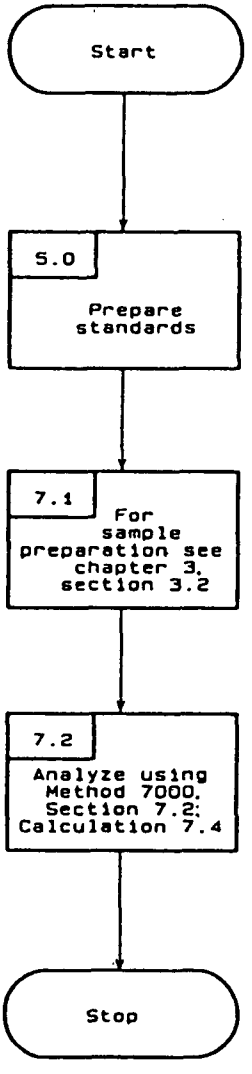
9.1 Precision and accuracy data are not available at this time.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 5-100 ug/L.
Detection limit: 1 ug/L.

10.0 REFERENCES

1. Application of Matrix-Modification in Determination of Thallium in Wastewater by Graphite-Furnace Atomic-Absorption Spectrometry, Talanta, 31(2) (1984), pp. 150-152.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2; Calculation 7.4
Stop

METHOD 7870

TIN (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Tin hollow cathode lamp.**
4.2.2 **Wavelength:** 286.3 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Nitrous oxide.
4.2.5 **Type of flame:** Fuel rich.
4.2.6 **Background correction:** Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g of tin metal (analytical reagent grade) in 100 mL of concentrated HCl and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

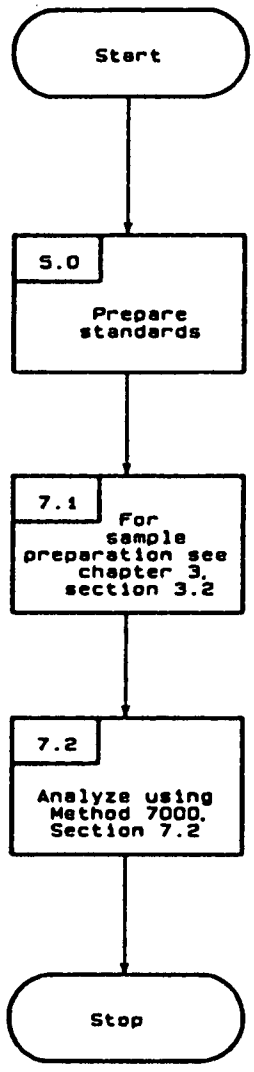
9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 10-300 mg/L with a wavelength of 286.3 nm.
Sensitivity: 4 mg/L.
Detection limit: 0.8 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 4, 20, and 60 mg/L gave standard deviations of ±0.25, ±0.5, and ±0.5, respectively. Recoveries at these levels were 96%, 101%, and 101%, respectively.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 282.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7910

VANADIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction may be required.

3.3 High concentrations of aluminum or titanium, or the presence of Bi, Cr, Co, Fe, acetic acid, phosphoric acid, surfactants, detergents, or alkali metals, may interfere. The interference can be controlled by adding 1,000 mg/L aluminum to samples and standards.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Vanadium hollow cathode lamp.**
4.2.2 **Wavelength:** 318.4 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Nitrous oxide.
4.2.5 **Type of flame:** Fuel rich.
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.7854 g of vanadium pentoxide, V_2O_5 (analytical reagent grade), in 10 mL of concentrated nitric acid and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

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5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing. In addition, 2 mL of the aluminum nitrate solution described in Paragraph 5.2.3 should be added to each 100 mL of standards and samples.

5.2.3 **Aluminum nitrate solution:** Dissolve 139 g aluminum nitrate ($Al[NO_3]_3 \cdot 9H_2O$) in 150 mL Type II water; heat to complete dissolution. Allow to cool and dilute to 200 mL with Type II water. All samples and standards should contain 2 mL of this solution per 100 mL.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

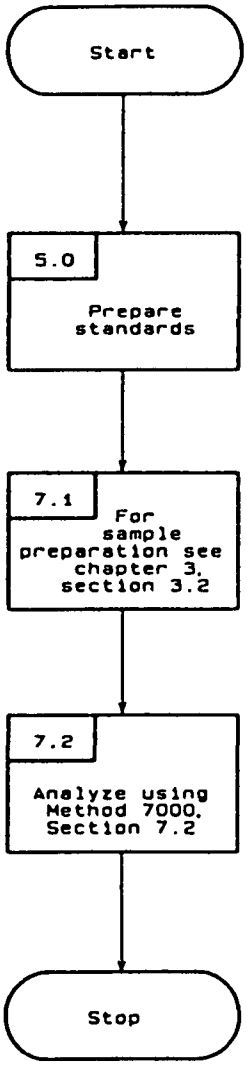
Optimum concentration range: 2-100 mg/L with a wavelength of 318.4 nm.
Sensitivity: 0.8 mg/L.
Detection limit: 0.2 mg/L.

9.2 In a single laboratory), analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 2, 10, and 50 mg/L gave standard deviations of ±0.1, ±0.1, and ±0.2, respectively. Recoveries at these levels were 100%, 95%, and 97%, respectively.

9.3 For concentrations of vanadium below 0.5 mg/L, the furnace technique (Method 7911) is recommended.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 286.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7911

VANADIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction is required.

3.3 Vanadium is refractory and prone to form carbides. Consequently, memory effects are common, and care should be taken to clean the furnace before and after analysis.

3.4 Nitrogen should not be used as a purge gas.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Drying time and temp:** 30 sec at 125°C.
4.2.2 **Ashing time and temp:** 30 sec at 1400°C.
4.2.3 **Atomizing time and temp:** 15 sec at 2800°C.
4.2.4 **Purge gas:** Argon (nitrogen should not be used).
4.2.5 **Wavelength:** 318.4 nm.
4.2.6 **Background correction:** Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.7854 g of vanadium pentoxide, V_2O_5 (analytical reagent grade), in 10 mL of concentrated nitric acid and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

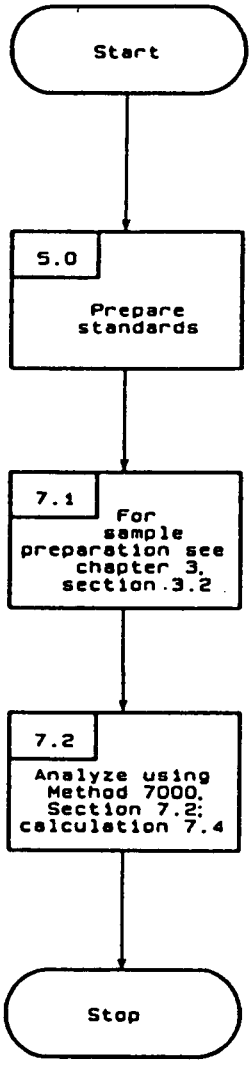
9.1 Precision and accuracy data are available in Method 286.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 10-200 ug/L.
Detection limit: 4 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 286.2.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2; calculation 7.4
Stop

METHOD 7950

ZINC (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 High levels of silicon, copper, or phosphate may interfere. Addition of strontium (1,500 mg/L) removes the copper and phosphate interference.

3.3 Zinc is a universal contaminant, and great care should be taken to avoid contamination.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Zinc hollow cathode lamp.**
4.2.2 **Wavelength:** 213.9 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Oxidizing (fuel lean).
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g zinc metal (analytical reagent grade) in 10 mL of concentrated nitric acid and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

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5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

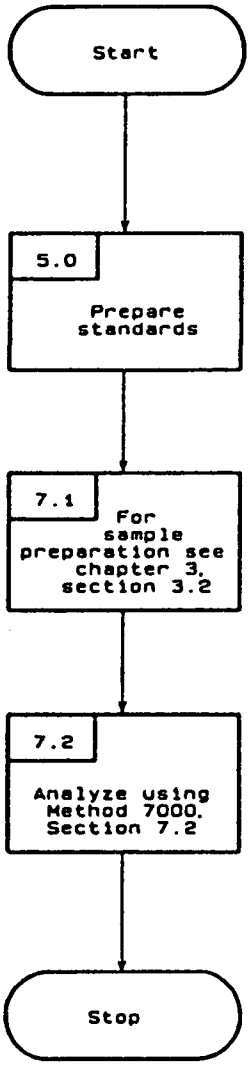
Optimum concentration range: 0.05-1 mg/L with a wavelength of 213.9 nm.
Sensitivity: 0.02 mg/L.
Detection limit: 0.005 mg/L.

9.2 For concentrations of zinc below 0.01 mg/L, the furnace technique (Method 7951) is recommended.

9.3 Precision and accuracy data are available in Method 289.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 289.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

APPENDIX

COMPANY REFERENCES

The following listing of frequently-used addresses is provided for the convenience of users of this manual. No endorsement is intended or implied.

Ace Glass Company
1342 N.W. Boulevard
P.O. Box 688
Vineland, NJ 08360
(609) 692-3333

Aldrich Chemical Company
Department T
P.O. Box 355
Milwaukee, WI 53201

Alpha Products
5570 - T W. 70th Place
Chicago, IL 60638
(312) 586-9810

Barneby and Cheney Company
E. 8th Avenue and N. Cassidy Street
P.O. Box 2526
Columbus, OH 43219
(614) 258-9501

Bio - Rad Laboratories
2200 Wright Avenue
Richmond, CA 94804
(415) 234-4130

Burdick & Jackson Lab Inc.
1953 S. Harvey Street
Muskegon, MO 49442

Calgon Corporation
P.O. Box 717
Pittsburgh, PA 15230
(412) 777-8000

Conostan Division
Conoco Speciality Products, Inc.
P.O. Box 1267
Ponca City, OK 74601
(405) 767-3456

Corning Glass Works
Houghton Park
Corning, NY 14830
(315) 974-9000

Dohrmann, Division of Xertex Corporation
3240 - T Scott Boulevard
Santa Clara, CA 95050
(408) 727-6000
(800) 538-7708

E. M. Laboratories, Inc.
500 Executive Boulevard
Elmsford, NY 10523

Fisher Scientific Co.
203 Fisher Building
Pittsburgh, PA 15219
(412) 562-8300

General Electric Corporation
3135 Easton Turnpike
Fairfield, CT 06431
(203) 373-2211

Graham Manufactory Co., Inc.
20 Florence Avenue
Batavia, NY 14020
(716) 343-2216

Hamilton Industries
1316 18th Street
Two Rivers, WI 54241
(414) 793-1121

ICN Life Sciences Group
3300 Hyland Avenue
Costa Mesa, CA 92626

Johns - Manville Corporation
P.O. Box 5108
Denver, CO 80217

Kontes Glass Company
8000 Spruce Street
Vineland, NJ 08360

Millipore Corporation
80 Ashby Road
Bedford, MA 01730
(617) 275-9200
(800) 225-1380

National Bureau of Standards
U.S. Department of Commerce
Washington, DC 20234
(202) 921-1000

Pierce Chemical Company
Box 117
Rockford, IL 61105
(815) 968-0747

Scientific Glass and Instrument, Inc.
7246 - T Wynnwood
P.O. Box 6
Houston, TX 77001
(713) 868-1481

Scientific Products Company
1430 Waukegon Road
McGaw Park, IL 60085
(312) 689-8410

Spex Industries
3880 - T and Park Avenue
Edison, NJ 08820

Waters Associates
34 - T Maple Street
Milford, MA 01757
(617) 478-2000
(800) 252-4752

Whatman Laboratory Products, Inc.
Clifton, NJ 07015
(201) 773-5800

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United States
Environmental Protection
Agency

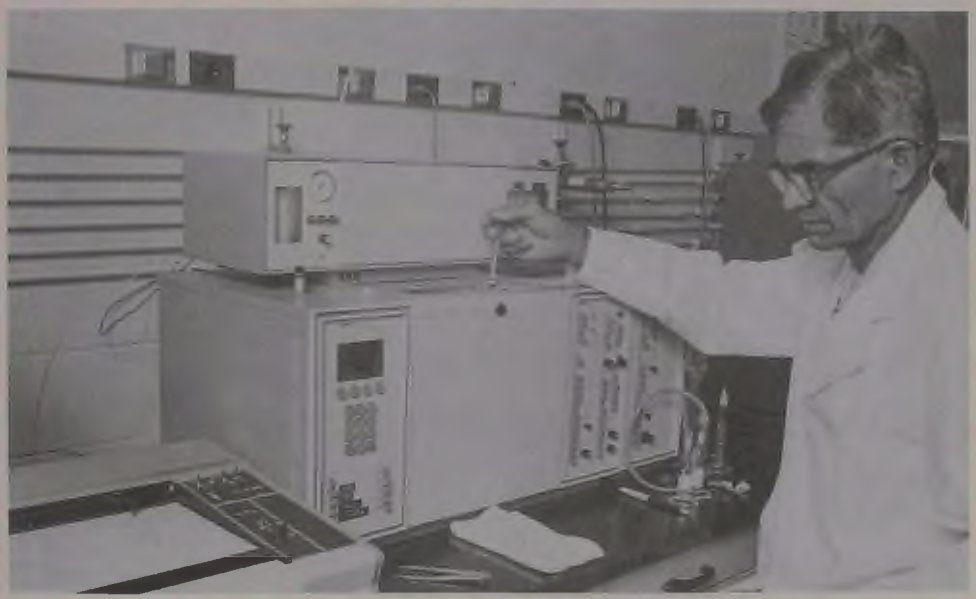
Office of Solid Waste
and Emergency Response
Washington, DC 20460

November 1986
SW-846
Third Edition

Solid Waste

Test Methods for Evaluating Solid Waste

Volume IB: Laboratory Manual Physical/Chemical Methods



ABSTRACT

This manual provides test procedures which may be used to evaluate those properties of a solid waste which determine whether the waste is a hazardous waste within the definition of Section 3001 of the Resource Conservation and Recovery Act (PL 94-580). These methods are approved for obtaining data to satisfy the requirement of 40 CFR Part 261, Identification and Listing of Hazardous Waste. This manual encompasses methods for collecting representative samples of solid wastes, and for determining the reactivity, corrosivity, ignitability, and composition of the waste and the mobility of toxic species present in the waste.

VOLUME ONE,

SECTION B

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Date September 1986

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METHOD INDEX AND CONVERSION TABLE

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0010	Ten	0010	0
0020	Ten	0020	0
0030	Ten	0030	0
1010	Eight (8.1)	1010	0
1020	Eight (8.1)	1020	0
1110	Eight (8.2)	1110	0
1310	Eight (8.4)	1310	0
1320	Six	1320	0
1330	Six	1330	0
3005	Three	3005	0
3010	Three	3010	0
3020	Three	3020	0
3040	Three	3040	0
3050	Three	3050	0
3500	Four (4.2.1)	None (new method)	0
3510	Four (4.2.1)	3510	0
3520	Four (4.2.1)	3520	0
3540	Four (4.2.1)	3540	0
3550	Four (4.2.1)	3550	0
3580	Four (4.2.1)	None (new method)	0
3600	Four (4.2.2)	None (new method)	0
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3611	Four (4.2.2)	3570	0
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3640	Four (4.2.2)	None (new method)	0
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3660	Four (4.2.2)	None (new method)	0
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7000	Three	7000	0
7020	Three	7020	0

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Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
7040	Three	7040	0
7041	Three	7041	0
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7741	Three	7741	0
7760	Three	7760	0
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Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
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7841	Three	7841	0
7870	Three	7870	0
7910	Three	7910	0
7911	Three	7911	0
7950	Three	7950	0
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8140	Four (4.3.1)	8140	0
8150	Four (4.3.1)	8150	0
8240	Four (4.3.2)	8240	0
8250	Four (4.3.2)	8250	0
8270	Four (4.3.2)	8270	0
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9022	Five	9022	0
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9038	Five	9038	0
9040	Six	9040	0
9041	Six	9041	0
9045	Six	9045	0
9050	Six	9050	0

Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
9060	Five	9060	0
9065	Five	9065	0
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9071	Five	9071	0
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9090	Six	9090	0
9095	Six	9095	0
9100	Six	9100	0
9131	Five	9131	0
9132	Five	9132	0
9200	Five	9200	0
9250	Five	9250	0
9251	Five	9251	0
9252	Five	9252	0
9310	Six	9310	0
9315	Six	9315	0
9320	Five	9320	0
HCN Test Method	Seven	HCN Test Method	0
H_2S Test Method	Seven	H_2S Test Method	0

PURPOSE OF THE MANUAL

Test Methods for Evaluating Solid Waste (SW-846) is intended to provide a unified, up-to-date source of information on sampling and analysis related to compliance with RCRA regulations. It brings together into one reference all sampling and testing methodology approved by the Office of Solid Waste for use in implementing the RCRA regulatory program. The manual provides methodology for collecting and testing representative samples of waste and other materials to be monitored. Aspects of sampling and testing covered in SW-846 include quality control, sampling plan development and implementation, analysis of inorganic and organic constituents, the estimation of intrinsic physical properties, and the appraisal of waste characteristics.

The procedures described in this manual are meant to be comprehensive and detailed, coupled with the realization that the problems encountered in sampling and analytical situations require a certain amount of flexibility. The solutions to these problems will depend, in part, on the skill, training, and experience of the analyst. For some situations, it is possible to use this manual in rote fashion. In other situations, it will require a combination of technical abilities, using the manual as guidance rather than in a step-by-step, word-by-word fashion. Although this puts an extra burden on the user, it is unavoidable because of the variety of sampling and analytical conditions found with hazardous wastes.

ORGANIZATION AND FORMAT

This manual is divided into two volumes. Volume I focuses on laboratory activities and is divided for convenience into three sections. Volume IA deals with quality control, selection of appropriate test methods, and analytical methods for metallic species. Volume IB consists of methods for organic analytes. Volume IC includes a variety of test methods for miscellaneous analytes and properties for use in evaluating the waste characteristics. Volume II deals with sample acquisition and includes quality control, sampling plan design and implementation, and field sampling methods. Included for the convenience of sampling personnel are discusssions of the ground water, land treatment, and incineration monitoring regulations.

Volume I begins with an overview of the quality control precedures to be imposed upon the sampling and analytical methods. The quality control chapter (Chapter One) and the methods chapters are interdependent. The analytical procedures cannot be used without a thorough understanding of the quality control requirements and the means to implement them. This understanding can be achieved only be reviewing Chapter One and the analytical methods together. It is expected that individual laboratories, using SW-846 as the reference

source, will select appropriate methods and develop a standard operating procedure (SOP) to be followed by the laboratory. The SOP should incorporate the pertinent information from this manual adopted to the specific needs and circumstances of the individual laboratory as well as to the materials to be evaluated.

The method selection chapter (Chapter Two) presents a comprehensive discussion of the application of these methods to various matrices in the determination of groups of analytes or specific analytes. It aids the chemist in constructing the correct analytical method from the array of procedures which may cover the matrix/analyte/concentration combination of interests. The section discusses the objective of the testing program and its relationship to the choice of an analytical method. Flow charts are presented along with tables to guide in the selection of the correct analytical procedures to form the appropriate method.

The analytical methods are separated into distinct procedures describing specific, independent analytical operations. These include extraction, digestion, cleanup, and determination. This format allows linking of the various steps in the analysis according to: the type of sample (e.g., water, soil, sludge, still bottom); analytes(s) of interest; needed sensitivity; and available analytical instrumentation. The chapters describing Miscellaneous Test Methods and Properties, however, give complete methods which are not amenable to such segmentation to form discrete procedures.

The introductory material at the beginning of each section containing analytical procedures presents information on sample handling and preservation, safety, and sample preparation.

Part II of Volume I (Chapters Seven and Eight) describes the characteristics of a waste. Sections following the regulatory descriptions contain the methods used to determine if the waste is hazardous because it exhibits a particular characteristic.

Volume II gives background information on statistical and nonstatistical aspects of sampling. It also presents practical sampling techniques appropriate for situations presenting a variety of physical conditions.

A discussion of the regulatory requirements with respect to several monitoring categories is also given in this volume. These include ground water monitoring, land treatment, and incineration. The purpose of this guidance is to orient the user to the objective of the analysis, and to assist in developing data quality objectives, sampling plans, and laboratory SOP's.

Significant interferences, or other problems, may be encountered with certain samples. In these situations, the analyst is advised to contact the Chief, Methods Section (WH-562B) Technical Assessment Branch, Office of Solid Waste, US EPA, Washington, DC 20460 (202-382-4761) for assistance. The manual is intended to serve all those with a need to evaluate solid waste. Your comments, corrections, suggestions, and questions concerning any material contained in, or omitted from, this manual will be gratefully appreciated. Please direct your comments to the above address.

CHAPTER ONE, REPRINTED

QUALITY CONTROL

1.1 INTRODUCTION

Appropriate use of data generated under the great range of analytical conditions encountered in RCRA analyses requires reliance on the quality control practices incorporated into the methods and procedures. The Environmental Protection Agency generally requires using approved methods for sampling and analysis operations fulfilling regulatory requirements, but the mere approval of these methods does not guarantee adequate results. Inaccuracies can result from many causes, including unanticipated matrix effects, equipment malfunctions, and operator error. Therefore, the quality control component of each method is indispensable.

The data acquired from quality control procedures are used to estimate and evaluate the information content of analytical data and to determine the necessity or the effect of corrective action procedures. The means used to estimate information content include precision, accuracy, detection limit, and other quantifiable and qualitative indicators.

1.1.1 Purpose of this Chapter

This chapter defines the quality control procedures and components that are mandatory in the performance of analyses, and indicates the quality control information which must be generated with the analytical data. Certain activities in an integrated program to generate quality data can be classified as management (QA) and other as functional (QC). The presentation given here is an overview of such a program.

The following sections discuss some minimum standards for QA/QC programs. The chapter is not a guide to constructing quality assurance project plans, quality control programs, or a quality assurance organization. Generators who are choosing contractors to perform sampling or analytical work, however, should make their choice only after evaluating the contractor's QA/QC program against the procedures presented in these sections. Likewise, laboratories that sample and/or analyze solid wastes should similarily evaluate their QA/QC programs.

Most of the laboratories who will use this manual also carry out testing other than that called for in SW-846. Indeed, many user laboratories have multiple mandates, including analyses of drinking water, wastewater, air and industrial hygiene samples, and process samples. These laboratories will, in most cases, already operate under an organizational structure that includes QA/QC. Regardless of the extent and history of their programs, the users of this manual should consider the development, status, and effectiveness of their QA/QC program in carrying out the testing described here.

1.1.2 Program Design

The initial step for any sampling or analytical work should be strictly to define the program goals. Once the goals have been defined, a program must be designed to meet them. QA and QC measures will be used to monitor the program and to ensure that all data generated are suitable for their intended use. The responsibility of ensuring that the QA/QC measures are properly employed must be assigned to a knowledgeable person who is not directly involved in the sampling or analysis.

One approach that has been found to provide a useful structure for a QA/QC program is the preparation of both general program plans and project-specific QA/QC plans.

The program plan for a laboratory sets up basic laboratory policies, including QA/QC, and may include standard operating procedures for specific tests. The program plan serves as an operational charter for the laboratory, defining its purposes, its organization and its operating principles. Thus, it is an orderly assemblage of management policies, objectives, principles, and general procedures describing how an agency or laboratory intends to produce data of known and accepted quality. The elements of a program plan and its preparation are described in QAMS-004/80 (see References, Section 1.6).

Project-specific QA/QC plans differ from program plans in that specific details of a particular sampling/analysis program are addressed. For example, a program plan might state that all analyzers will be calibrated according to a specific protocol given in written standard operating procedures for the laboratory (SOP), while a project plan would state that a particular protocol will be used to calibrate the analyzer for a specific set of analyses that have been defined in the plan. The project plan draws on the program plan or its basic structure and applies this management approach to specific determinations. A given agency or laboratory would have only one quality assurance program plan, but would have a quality assurance project plan for each of its projects. The elements of a project plan and its preparation are described in QAMS/005/80 (see References, Section 1.6) and are listed in Figure 1-1.

Some organizations may find it inconvenient or even unnecessary to prepare a new project plan for each new set of analyses, especially analytical laboratories which receive numerous batches of samples from various customers within and outside their organizations. For these organizations, it is especially important that adequate QA management structures exist and that any procedures used exist as standard operating procedures (SOP), written documents which detail an operation, analysis or action whose mechanisms are thoroughly prescribed and which is commonly accepted as the method for performing certain routine or repetitive tasks. Having copies of SW-846 and all its referenced documents in one's laboratory is not a substitute for having in-house versions of the methods written to conform to specific instrumentation, data needs, and data quality requirements.

FIGURE 1-1

ESSENTIAL ELEMENTS OF A QA PROJECT PLAN

1. Title Page
2. Table of Contents
3. Project Description
4. Project Organization and Responsibility
5. QA Objectives
6. Sampling Procedures
7. Sample Custody
8. Calibration Procedures and Frequency
9. Analytical Procedures
10. Data Reduction, Validation, and Reporting
11. Internal Quality Control Checks
12. Performance and System Audits
13. Preventive Maintenance
14. Specific Routine Procedures Used to Assess Data Precision, Accuracy, and Completeness
15. Corrective Action
16. Quality Assurance Reports to Management

1.1.3 Organization and Responsibility

As part of any measurement program, activities for the data generators, data reviewers/approvers, and data users/requestors must be clearly defined. While the specific titles of these individuals will vary among agencies and laboratories, the most basic structure will include at least one representative of each of these three types. The data generator is typically the individual who carries out the analyses at the direction of the data user/requestor or a designate within or outside the laboratory. The data reviewer/approver is responsible for ensuring that the data produced by the data generator meet agreed-upon specifications.

Responsibility for data review is sometimes assigned to a "Quality Assurance Officer" or "QA Manager." This individual has broad authority to approve or disapprove project plans, specific analyses and final reports. The QA Officer is independent from the data generation activities. In general, the QA Officer is responsible for reviewing and advising on all aspects of QA/QC, including:

Assisting the data requestor in specifying the QA/QC procedure to be used during the program;

Making on-site evaluations and submitting audit samples to assist in reviewing QA/QC procedures; and,

f problems are detected, making recommendations to the data requestor and upper corporate/institutional management to ensure that appropriate corrective actions are taken.

In programs where large and complex amounts of data are generated from both field and laboratory activities, it is helpful to designate sampling monitors, analysis monitors, and quality control/data monitors to assist in carrying out the program or project.

The sampling monitor is responsible for field activities. These include:

Determining (with the analysis monitor) appropriate sampling equipment and sample containers to minimize contamination;

Ensuring that samples are collected, preserved, and transported as specified in the workplan; and

Checking that all sample documentation (labels, field notebooks, chain-of-custody records, packing lists) is correct and transmitting that information, along with the samples, to the analytical laboratory.

The analysis monitor is responsible for laboratory activities. These include:

Training and qualifying personnel in specified laboratory QC and analytical procedures, prior to receiving samples;

Receiving samples from the field and verifying that incoming samples correspond to the packing list or chain-of-custody sheet; and

Verifying that laboratory QC and analytical procedures are being followed as specified in the workplan, reviewing sample and QC data during the course of analyses, and, if questionable data exist, determining which repeat samples or analyses are needed.

The quality control and data monitor is responsible for QC activities and data management. These include:

Maintaining records of all incoming samples, tracking those samples through subsequent processing and analysis, and, ultimately, appropriately disposing of those samples at the conclusion of the program;

Preparing quality control samples for analysis prior to and during the program;

Preparing QC and sample data for review by the analysis coordinator and the program manager; and

Preparing QC and sample data for transmission and entry into a computer data base, if appropriate.

1.1.4 Performance and Systems Audits

The QA Officer may carry out performance and/or systems audits to ensure that data of known and defensible quality are produced during a program,.

Systems audits are qualitative evaluations of all components of field and laboratory quality control measurement systems. They determine if the measurement systems are being used appropriately. The audits may be carried out before all systems are operational, during the program, or after the completion of the program. Such audits typically involve a comparison of the activities given in the QA/QC plan with those actually scheduled or performed. A special type of systems audit is the data management audit. This audit addresses only data collection and management activities.

The performance audit is a quantitative evaluation of the measurement systems of a program. It requires testing the measurement systems with samples of known composition or behavior to evaluate precision and accuracy. The performance audit is carried out by or under the auspices of the QA Officer without the knowledge of the analysts. Since this is seldom achievable, many variations are used that increase the awareness of the analyst as to the nature of the audit material.

1.1.5 Corrective Action

Corrective action procedures should be addressed in the program plan, project, or SOP. These should include the following elements:

The EPA predetermined limits for data acceptability beyond which corrective action is required;

Procedures for corrective action; and,

For each measurement system, identification of the individual responsible for initiating the corrective action and the individual responsible for approving the corrective action, if necessary.

The need for corrective action may be identified by system or performance audits or by standard QC procedures. The essential steps in the corrective action system are:

Identification and definition of the problem;

Assignment of responsibility for investigating the problem;

Investigation and determination of the cause of the problem;

Determination of a corrective action to eliminate the problem;

Assigning and accepting responsibility for implementing the corrective action;

Implementing the corrective action and evaluating its effectiveness; and

Verifying that the corrective action has eliminated the problem.

The QA Officer should ensure that these steps are taken and that the problem which led to the corrective action has been resolved.

1.1.6 QA/QC Reporting to Management

QA Project Program or Plans should provide a mechanism for periodic reporting to management (or to the data user) on the performance of the measurement system and the data quality. Minimally, these reports should include:

Periodic assessment of measurement quality indicators, i.e., data accuracy, precision and completeness;

Results of performance audits;

Results of system audits; and

Significant QA problems and recommended solutions.

The individual responsible within the organization structure for preparing the periodic reports should be identified in the organizational or management plan. The final report for each project should also include a separate QA section which summarizes data quality information contained in the periodic reports.

Other guidance on quality assurance management and organizations is available from the Agency and professional organizations such as ASTM, AOAC, APHA and FDA.

1.1.7 Quality Control Program for the Analysis of RCRA Samples

An analytical quality control program develops information which can be used to:

Evaluate the accuracy and precision of analytical data in order to establish the quality of the data;

Provide an indication of the need for corrective actions, when comparison with existing regulatory or program criteria or data trends shows that activities must be changed or monitored to a different degree; and

To determine the effect of corrective actions.

1.1.8 Definitions

ACCURACY: Accuracy means the nearness of a result or the mean ($\bar{x}$) of a set of results to the true value. Accuracy is assessed by means of reference samples and percent recoveries.

ANALYTICAL BATCH: The basic unit for analytical quality control is the analytical batch. The analytical batch is defined as samples which are analyzed together with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar composition.

BLANK: A blank is an artificial sample designed to monitor the introduction of artifacts into the process. For aqueous samples, reagent water is used as a blank matrix; however, a universal blank matrix does not exist for solid samples, and therefore, no matrix is used. The blank is taken through the appropriate steps of the process.
A reagent blank is an aliquot of analyte-free water or solvent analyzed with the analytical batch. Field blanks are aliquots of analyte-free water or solvents brought to the field in sealed containers and transported back to the

laboratory with the sample containers. Trip blanks and equipment blanks are two specific types of field blanks. Trip blanks are not opened in the field. They are a check on sample contamination originating from sample transport, shipping and from site conditions. Equipment blanks are opened in the field and the contents are poured appropriately over or through the sample collection device, collected in a sample container, and returned to the laboratory as a sample. Equipment blanks are a check on sampling device cleanliness.

CALIBRATION CHECK: Verification of the ratio of instrument response to analyte amount, a calibration check, is done by analyzing for analyte standards in an appropriate solvent. Calibration check solutions are made from a stock solution which is different from the stock used to prepare standards.

CHECK SAMPLE: A blank which has been spiked with the analyte(s) from an independent source in order to monitor the execution of the analytical method is called a check sample. The level of the spike shall be at the regulatory action level when applicable. Otherwise, the spike shall be at 5 times the estimate of the quantification limit. The matrix used shall be phase matched with the samples and well characterized: for an example, reagent grade water is appropriate for an aqueous sample.

ENVIRONMENTAL SAMPLE: An environmental sample or field sample is a representative sample of any material (aqueous, nonaqueous, or multimedia) collected from any source for which determination of composition or contamination is requested or required. For the purposes of this manual, environmental samples shall be classified as follows:

Surface Water and Ground Water;

Drinking Water -- delivered (treated or untreated) water designated as potable water;

Water/Wastewater -- raw source waters for public drinking water supplies, ground waters, municipal influents/effluents, and industrial influents/effluents;

Sludge -- municipal sludges and industrial sludges;

Waste -- aqueous and nonaqueous liquid wastes, chemical solids, contaminated soils, and industrial liquid and solid wastes.

MATRIX/SPIKE-DUPLICATE ANALYSIS: In matrix/spike duplicate analysis, predetermined quantities of stock solutions of certain analytes are added to a added to a sample matrix prior to sample extraction/digestion and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected. The relative percent difference between the samples is calculated and used to assess analytical precision. The concentration of the spike should be at the regulatory standard level or the estimated or actual method quantification limit. When the concentration of the analyte in the sample is greater than 0.1%, no spike of the analyte is necessary.

MQL: The method quantification limit (MQL) is the minimum concentration of a substance that can be measured and reported.

PRECISION: Precision means the measurement of agreement of a set of replicate results among themselves without assumption of any prior information as to the true result. Precision is assessed by means of duplicate/replicate sample analysis.

PQL: The practical quantitation limit (PQL) is the lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions.

RCRA: The Resource Conservation and Recovery Act.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonomous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REPLICATE SAMPLE: A replicate sample is a sample prepared by dividing a sample into two or more separate aliquots. Duplicate samples are considered to be two replicates.

STANDARD CURVE: A standard curve is a curve which plots concentrations of known analyte standard versus the instrument response to the analyte.

SURROGATE: Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, standards, samples and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

WATER: Reagent, analyte-free, or laboratory pure water means distilled or deionized water or Type II reagent water which is free of contaminants that may interfere with the analytical test in question.

1.2 QUALITY CONTROL

The procedures indicated below are to be performed for all analyses. Specific instructions relevant to particular analyses are given in the pertinent analytical procedures.

1.2.1 Field Quality Control

The sampling component of the Quality Assurance Project Plan (QAPP) shall include:

Reference to or incorporation of accepted sampling techniques in the sampling plan;

Procedures for documenting and justifying any field actions contrary to the QAPP;

Documentation of all pre-field activities such as equipment check-out, calibrations, and container storage and preparation;

Documentation of field measurement quality control data (quality control procedures for such measurements shall be equivalent to corresponding laboratory QC procedures);

Documentation of field activities;

Documentation of post-field activities including sample shipment and receipt, field team de-briefing and equipment check-in;

Generation of quality control samples including duplicate samples, field blanks, equipment blanks, and trip blanks; and

The use of these samples in the context of data evaluation, with details of the methods employed (including statistical methods) and of the criteria upon which the information generated will be judged.

1.2.2 Analytical Quality Control

A quality control operation or component is only useful if it can be measured or documented. The following components of analytical quality control are related to the analytical batch. The procedures described are intended to be applied to chemical analytical procedures; although the principles are applicable to radio-chemical or biological analysis, the procedures may not be directly applicable to such techniques.

All quality control data and records required by this section shall be retained by the laboratory and shall be made available to the data requestor as appropriate. The frequencies of these procedures shall be as stated below or at least once with each analytical batch.

1.2.2.1 Spikes, Blanks and Duplicates

General Requirements

These procedures shall be performed at least once with each analytical batch with a minimum of once per twenty samples.

1.2.2.1.1 Duplicate Spike

A split/spiked field sample shall be analyzed with every analytical batch or once in twenty samples, whichever is the greater frequency. Analytes stipulated by the analytical method, by applicable regulations, or by other specific requirements must be spiked into the sample. Selection of the sample to be spiked and/or split depends on the information required and the variety of conditions within a typical matrix. In some situations, requirements of the site being sampled may dictate that the sampling team select a sample to be spiked and split based on a pre-visit evaluation or the on-site inspection. This does not preclude the laboratory's spiking a sample of its own selection as well. In other situations the laboratory may select the appropriate sample. The laboratory's selection should be guided by the objective of spiking, which is to determine the extent of matrix bias or interference on analyte recovery and sample-to-sample precision. For soil/sediment samples, spiking is performed at approximately 3 ppm and, therefore, compounds in excess of this concentration in the sample may cause interferences for the determination of the spiked analytes.

1.2.2.1.2 Blanks

Each batch shall be accompanied by a reagent blank. The reagent blank shall be carried through the entire analytical procedure.

1.2.2.1.3 Field Samples/Surrogate Compounds

Every blank, standard, and environmental sample (including matrix spike/matrix duplicate samples) shall be spiked with surrogate compounds prior to purging or extraction. Surrogates shall be spiked into samples according to the appropriate analytical methods. Surrogate spike recoveries shall fall within the control limits set by the laboratory (in accordance with procedures specified in the method or within ±20%) for samples falling within the quantification limits without dilution. Dilution of samples to bring the analyte concentration into the linear range of calibration may dilute the surrogates below the quantification limit; evaluation of analytical quality then will rely on the quality control embodied in the check, spiked and duplicate spiked samples.

1.2.2.1.4 Check Sample

Each analytical batch shall contain a check sample. The analytes employed shall be a representative subset of the analytes to be determined. The concentrations of these analytes shall approach the estimated quantification limit in the matrix of the check sample. In particular, check samples for metallic analytes shall be matched to field samples in phase and in general matrix composition.

1.2.2.2 Clean-Ups

Quality control procedures described here are intended for adsorbent chromatography and back extractions applied to organic extracts. All batches of adsorbents (Florisil, alumina, silica gel, etc.) prepared for use shall be checked for analyte recovery by running the elution pattern with standards as a column check. The elution pattern shall be optimized for maximum recovery of analytes and maximum rejection of contaminants.

1.2.2.2.1 Column Check Sample

The elution pattern shall be reconfirmed with a column check of standard compounds after activating or deactivating a batch of adsorbent. These compounds shall be representative of each elution fraction. Recovery as specified in the methods is considered an acceptable column check. A result lower than specified indicates that the procedure is not acceptable or has been misapplied.

1.2.2.2.2 Column Check Sample Blank

The check blank shall be run after activating or deactivating a batch of adsorbent.

1.2.2.3 Determinations

1.2.2.3.1 Instrument Adjustment: Tuning, Alignment, etc.

Requirements and procedures are instrument- and method-specific. Analytical instrumentation shall be tuned and aligned in accordance with requirements which are specific to the instrumentation procedures employed. Individual determinative procedures shall be consulted. Criteria for initial conditions and for continuing confirmation conditions for methods within this manual are found in the appropriate procedures.

1.2.2.3.2 Calibration

Analytical instrumentation shall be calibrated in accordance with requirements which are specific to the instrumentation and procedures employed. Introductory Methods 7000 and 8000 and appropriate analytical procedures shall be consulted for criteria for initial and continuing calibration.

1.2.2.3.3 Additional QC Requirements for Inorganic Analysis

Standard curves used in the determination of inorganic analytes shall be prepared as follows:

Standard curves derived from data consisting of one reagent blank and four concentrations shall be prepared for each analyte. The response for each prepared standard shall be based upon the average of three replicate readings of each standard. The standard curve shall be used with each subsequent analysis provided that the standard curve is verified by using at least one reagent blank and one standard at a level normally encountered or expected in such samples. The response for each standard shall be based upon the average of three replicate readings of the standard. If the results of the verification are not within ±10% of the original curve, a new standard shall be prepared and analyzed. If the results of the second verification are not within ±10% of the original standard curve, a reference standard should be employed to determine if the discrepancy is with the standard or with the instrument. New standards should also be prepared on a quarterly basis at a minimum. All data used in drawing or describing the curve shall be so indicated on the curve or its description. A record shall be made of the verification.

Standard deviations and relative standard deviations shall be calculated for the percent recovery of analytes from the spiked sample duplicates and from the check samples. These values shall be established for the twenty most recent determinations in each category.

1.2.2.3.4 Additional Quality Control Requirements for Organic Analysis

The following requirements shall be applied to the analysis of samples by gas chromatography, liquid chromatography and gas chromatography/mass spectrometry.

The calibration of each instrument shall be verified at frequencies specified in the methods. A new standard curve must be prepared as specified in the methods.

The tune of each GC/MS system used for the determination of organic analytes shall be checked with 4-bromofluorobenzene (BFB) for determinations of volatiles and with decafluorotriphenylphosphine (DFTPP) for determinations of semi-volatiles. The required ion abundance criteria shall be met before determination of any analytes. If the system does not meet the required specification for one or more of the required ions, the instrument must be retuned and rechecked before proceeding with sample analysis. The tune performance check criteria must be achieved daily or for each 12 hour operating period, whichever is more frequent.

Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. Background subtraction

actions resulting in spectral distortions for the sole purpose of meeting special requirements are contrary to the objectives of Quality Assurance and are unacceptable.

For determinations by HPLC or GC, the instrument calibration shall be verified as specified in the methods.

1.2.2.3.5 Identification

Identification of all analytes must be accomplished with an authentic standard of the analyte. When authentic standards are not available, identification is tentative.

For gas chromatographic determinations of specific analytes, the relative retention time of the unknown must be compared with that of an authentic standard. For compound confirmation, a sample and standard shall be re-analyzed on a column of different selectivity to obtain a second characteristic relative retention time. Peaks must elute within daily retention time windows to be declared a tentative or confirmed identification.

For gas chromatographic/mass spectrometric determinations of specific analytes, the spectrum of the analyte should conform to a literature representation of the spectrum or to a spectrum of the authentic standard obtained after satisfactory tuning of the mass spectrometer and within the same twelve-hour working shift as the analytical spectrum. The appropriate analytical methods should be consulted for specific criteria for matching the mass spectra, relative response factors, and relative retention times to those of authentic standards.

1.2.2.3.6 Quantification

The procedures for quantification of analytes are discussed in the appropriate general procedures (7000, 8000) and the specific analytical methods.

In some situations in the course of determining metal analytes, matrix-matched calibration standards may be required. These standards shall be composed of the pure reagent, approximation of the matrix, and reagent addition of major interferents in the samples. This will be stipulated in the procedures.

Estimation of the concentration of an organic compound not contained within the calibration standard may be accomplished by comparing mass spectral response of the compound with that of an internal standard. The procedure is specified in the methods.

1.3 DETECTION LIMIT AND QUANTIFICATION LIMIT

The detection limit and quantification limit of analytes shall be evaluated by determining the noise level of response for each sample in the batch. If analyte is present, the noise level adjacent in retention time to the analyte peak may be used. For wave-length dispersive instrumentation, multiple determinations of digestates with no detectable analyte may be used to establish the noise level. The method of standard additions should then be used to determine the calibration curve using one digestate or extracted sample in which the analyte was not detected. The slope of the calibration curve, m, should be calculated using the following relations:

m = slope of calibration line

S_B = standard deviation of the average noise level

$MDL = KS_B/m$

For K = 3; MDL = method detection limit.

For K = 5; MQL = method quantitation limit.

1.4 DATA REPORTING

The requirement of reporting analytical results on a wet-weight or a dry-weight basis is dictated by factors such as: sample matrix; program or regulatory requirement; and objectives of the analysis.

Analytical results shall be reported with the percent moisture or percent solid content of the sample.

1.5 QUALITY CONTROL DOCUMENTATION

The following sections list the QC documentation which comprises the complete analytical package. This package should be obtained from the data generator upon request. These forms, or adaptations of these forms, shall be used by the data generator/reportor for inorganics (I), or for organics (O) or both (I/O) types of determinations.

1.5.1 Analytical Results (I/O: Form I)

Analyte concentration.

Sample weight.

Percent water (for non-aqueous samples when specified).

Final volume of extract or diluted sample.

Holding times (I: Form X).

1.5.2 Calibration (I: Form II; O: Form V, VI, VII, IX)

Calibration curve or coefficients of the linear equation which describes the calibration curve.

Correlation coefficient of the linear calibration.

Concentration/response data (or relative response data) of the calibration check standards, along with dates on which they were analytically determined.

1.5.3 Column Check (O: Form X)

Results of column chromatography check, with the chromatogram.

1.5.4 Extraction/Digestion (I/O: Form I)

Date of the extraction for each sample.

1.5.5 Surrogates (O: Form II)

Amount of surrogate spiked, and percent recovery of each surrogate.

1.5.6 Matrix/Duplicate Spikes (I: Form V, VI; O: Form III)

Amount spiked, percent recovery, and relative percent difference for each compound in the spiked samples for the analytical batch.

1.5.7 Check Sample (I: Form VII; O: Form VIII)

Amount spiked, and percent recovery of each compound spiked.

1.5.8 Blank (I: Form III; O: Form IV)

Identity and amount of each constituent.

1.5.9 Chromatograms (for organic analysis)

All chromatograms for reported results, properly labeled with:

- Sample identification
- Method identification
- Identification of retention time of analyte on the chromatograms.

1.5.10 Quantitative Chromatogram Report (O: Forms VIII, IX, X)

Retention time of analyte.

Amount injected.

Area of appropriate calculation of detection response.

Amount of analyte found.

Date and time of injection.

1.5.11 Mass Spectrum

Spectra of standards generated from authentic standards (one for each report for each compound detected).

Spectra of analytes from actual analyses.

Spectrometer identifier.

1.5.12 Metal Interference Check Sample Results (I: Form IV)

1.5.13 Detection Limit (I: Form VII; O: Form I)

Analyte detection limits with methods of estimation.

1.5.14 Results of Standard Additions (I: Form VIII)

1.5.15 Results of Serial Dilutions (I: Form IX)

1.5.16 Instrument Detection Limits (I: Form XI)

1.5.17 ICP Interelement Correction Factors and ICP Linear Ranges (when applicable) (I: Form XII, Form XIII).

1.6 REFERENCES

1. Guidelines and Specifications for Preparing Quality Assurance Program Plans, September 20, 1980, Office of Monitoring Systems and Quality Assurance, ORD, U.S. EPA, QAMS-004/80, Washington, DC 20460.

2. Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans, December 29, 1980, Office of Monitoring Systems and Quality Assurance, ORD, U.S. EPA, QAMS-005/80, Washington, DC 20460.

Date _____

COVER PAGE
INORGANIC ANALYSES DATA PACKAGE

Lab Name _____ Case No. _____

No. _____ Q.C. Report No. _____

Sample Numbers

EPA No.	Lab ID No.	EPA No.	Lab ID No.

Comments: _____

Form I

Sample No.

Date _____

INORGANIC ANALYSIS DATA SHEET

LAB NAME _____ CASE NO. _____

Lab Receipt Date _____

LAB SAMPLE ID. NO. _____ QC REPORT NO. _____

Elements Identified and Measured

Matrix: Water _____ Soil _____ Sludge _____ Other _____

ug/L or mg/kg dry weight (Circle One)

1.	Aluminum	13.	Magnesium
2.	Antimony	14.	Manganese
3.	Arsenic	15.	Mercury
4.	Barium	16.	Nickel
5.	Beryllium	17.	Potassium
6.	Cadmium	18.	Selenium
7.	Calcium	19.	Silver
8.	Chromium	20.	Sodium
9.	Cobalt	21.	Thallium
10.	Copper	22.	Vanadium
11.	Iron	23.	Zinc
12.	Lead	Precent Solids (%)	

Cyanide _____

Comments: _____

_____

_____

_____

Lab Manager _____

Revision 0
Date September 1986

Form II

Q. C. Report No. _____

INITIAL AND CONTINUING CALIBRATION VERIFICATION

LAB NAME _____ CASE NO. _____

DATE _____ UNITS: ug/L

Compound	Initial Calib.[1]			Continuing Calibration[2]					
Metals:	True Value	Found	%R	True Value	Found	%R	Found	%R	Method[4]
1. Aluminum									
2. Antimony									
3. Arsenic									
4. Barium									
5. Beryllium									
6. Cadmium									
7. Calcium									
8. Chromium									
9. Cobalt									
10. Copper									
11. Iron									
12. Lead									
13. Magnesium									
14. Manganese									
15. Mercury									
16. Nickel									
17. Potassium									
18. Selenium									
19. Silver									
20. Sodium									
21. Thallium									
22. Vanadium									
23. Zinc									
Other: _____									
Cyanide									

[1] Initial Calibration Source [2] Continuing Calibration Source _____

[4] Indicate Analytical Method Used: P - ICP; A - Flame AA; F - Furnace AA

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Form III

Q. C. Report No. _____

BLANKS

LAB NAME _____ CASE NO. _____

DATE _____ UNITS _____

Compound	Initial Calibration Blank Value	Continuing Calibration Blank Value 1	2	3	4	Preparation Blank Matrix: 1	Matrix: 2
Metals:							
1. Aluminum							
2. Antimony							
3. Arsenic							
4. Barium							
5. Beryllium							
6. Cadmium							
7. Calcium							
8. Chromium							
9. Cobalt							
10. Copper							
11. Iron							
12. Lead							
13. Magnesium							
14. Manganese							
15. Mercury							
16. Nickel							
17. Potassium							
18. Selenium							
19. Silver							
20. Sodium							
21. Thallium							
22. Vanadium							
23. Zinc							
Other:							
Cyanide							

[1] Reporting Units: aqueous, ug/L; solid mg/kg

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Form IV

Q. C. Report No. _____

ICP INTERFERENCE CHECK SAMPLE

LAB NAME _____ CASE NO. _____

Check Sample I.D. _____

DATE _____ Check Sample Source _____

Units: ug/L

Compound	Control Limits[1] Mean	Control Limits[1] Std. Dev.	True[2]	Initial Observed	Initial %R	Final Observed	Final %R
Metals:							
1. Aluminum							
2. Antimony							
3. Arsenic							
4. Barium							
5. Beryllium							
6. Cadmium							
7. Calcium							
8. Chromium							
9. Cobalt							
10. Copper							
11. Iron							
12. Lead							
13. Magnesium							
14. Manganese							
15. Mercury							
16. Nickel							
17. Potassium							
18. Selenium							
19. Silver							
20. Sodium							
21. Thallium							
22. Vanadium							
23. Zinc							
Other: _____							

[1] Mean value based on n = _____.

[2] True value of EPA ICP Interference Check Sample or contractor standard.

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Form V

Q. C. Report No. _____

SPIKE SAMPLE RECOVERY

LAB NAME _____ CASE NO. _____

Sample No. _____

DATE _____ Lab Sample ID No. _____

Units _____

Matrix _____

Compound	Control Limit %R	Spiked Sample Result (SSR)	Sample Result (SR)	Spiked Added (SA)	%R[1]
Metals:					
1. Aluminum					
2. Antimony					
3. Arsenic					
4. Barium					
5. Beryllium					
6. Cadmium					
7. Calcium					
8. Chromium					
9. Cobalt					
10. Copper					
11. Iron					
12. Lead					
13. Magnesium					
14. Manganese					
15. Mercury					
16. Nickel					
17. Potassium					
18. Selenium					
19. Silver					
20. Sodium					
21. Thallium					
22. Vanadium					
23. Zinc					
Other:					
Cyanide					

[1] %R = [(SSR - SR)/SA] x 100

"N" - out of control

"NR" - Not required

Comments: _____

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Form VI

Q. C. Report No. _____

DUPLICATES

LAB NAME _____ CASE NO. _____

Sample No. _____

DATE _____ Lab Sample ID No. _____

Units _____

Matrix _____

Compound	Control Limit[1]	Sample(S)	Duplicate(D)	RPD[2]
Metals:				
1. Aluminum				
2. Antimony				
3. Arsenic				
4. Barium				
5. Beryllium				
6. Cadmium				
7. Calcium				
8. Chromium				
9. Cobalt				
10. Copper				
11. Iron				
12. Lead				
13. Magnesium				
14. Manganese				
15. Mercury				
16. Nickel				
17. Potassium				
18. Selenium				
19. Silver				
20. Sodium				
21. Thallium				
22. Vanadium				
23. Zinc				
Other:				
Cyanide				

* Out of Control

[1] To be added at a later date.

[2] RPD = [|S - D|/((S + D)/2)] x 100

NC - Non calculable RPD due to value(s) less than CRDL

Form VII

Q.C. Report No. _____

INSTRUMENT DETECTION LIMITS AND

LABORATORY CONTROL SAMPLE

LAB NAME _____ CASE NO. _____ DATE _____

LCS NO. _____

Compound	Required Detection Limits (CRDL)-ug/l	Instrument Detection Limits (IDL)-ug/l ICP/AA ID# _____	Instrument Detection Limits (IDL)-ug/l Furnace ID# _____	Lab Control Sample ug/L mg/kg (circle one) True	Found	%R
Metals:						
1. Aluminum						
2. Antimony						
3. Arsenic						
4. Barium						
5. Beryllium						
6. Cadmium						
7. Calcium						
8. Chromium						
9. Cobalt						
10. Copper						
11. Iron						
12. Lead						
13. Magnesium						
14. Manganese						
15. Mercury						
16. Nickel						
17. Potassium						
18. Selenium						
19. Silver						
20. Sodium						
21. Thallium						
22. Vanadium						
23. Zinc						
Other: _____						
Cyanide		NR	NR			

NR - Not required

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Form VIII

Q.C. Report No. _____

STANDARD ADDITION RESULTS

LAB NAME _____ CASE NO. _____

DATE _____ UNITS: ug/L

EPA Sample #	Element	Matrix	0 ADD ABS.	1 ADD CON.	1 ADD ABS.[2]	2 ADD CON.	2 ADD ABS.[2]	3 ADD CON.	3 ADD ABS.[2]	FINAL CON.[3]	r*

[2] CON is the concentration added, ABS. is the instrument readout in absorbance or concentration.

[3] Concentration as determined by MSA

*"r" is the correlation coefficient.

+ - correlation coefficient is outside of control window of 0.995.

Revision 0
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Form IX

Q. C. Report No. _____

ICP SERIAL DILUTIONS

LAB NAME _____ CASE NO. _____

Sample No. _____

DATE _____ Lab Sample ID No. _____

Units: ug/L

Matrix _____

Compound	Initial Sample Concentration(I)	Serial Dilution[1] Result(S)	% Difference[2]
Metals:			
1. Aluminum			
2. Antimony			
3. Arsenic			
4. Barium			
5. Beryllium			
6. Cadmium			
7. Calcium			
8. Chromium			
9. Cobalt			
10. Copper			
11. Iron			
12. Lead			
13. Magnesium			
14. Manganese			
15. Nickel			
16. Potassium			
17. Selenium			
18. Silver			
19. Sodium			
20. Thallium			
21. Vanadium			
22. Zinc			
Other:			

[1] Diluted sample concentration corrected for 1:4 dilution (see Exhibit D)

[2] Percent Difference = $\frac{|I - S|}{I} \times 100$

NR - Not Required, initial sample concentration less than 10 times IDL

NA - Not Applicable, analyte not determined by ICP

Revision 0
Date September 1986

Form X

QC Report No. _____

HOLDING TIMES

LAB NAME _____

DATE _____ CASE NO. _____

EPA Sample No.	Matrix	Date Received	Mercury Prep Date	Mercury Holding Time[1] (Days)	CN Prep Date	CN Holding Time[1] (Days)

[1]Holding time is defined as number of days between the date received and the sample preparation date.

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Form XI

INSTRUMENT DETECTION LIMITS

LAB NAME _____ DATE _____

ICP/Flame AA (Circle One) Model Number _____ Furnace AA Number _____

Element	Wavelength (nm)	IDL (ug/L)	Element	Wavelength (nm)	IDL (ug/L)
1. Aluminum			13. Magnesium		
2. Antimony			14. Manganese		
3. Arsenic			15. Mercury		
4. Barium			16. Nickel		
5. Beryllium			17. Potassium		
6. Cadmium			18. Selenium		
7. Calcium			19. Silver		
8. Chromium			20. Sodium		
9. Cobalt			21. Thallium		
10. Copper			22. Vanadium		
11. Iron			23. Zinc		
12. Lead					

Footnotes:
- Indicate the instrument for which the IDL applies with a "P" (for ICP an "A" (for Flame AA), or an "F" (for Furnace AA) behind the IDL valu
- Indicate elements commonly run with background correction (AA) with a "B" behind the analytical wavelength.
- If more than one ICP/Flame or Furnace AA is used, submit separate Forms XI-XIII for each instrument.

COMMENTS: _____

_____

_____

_____

Lab Manager _____

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Form XII

ICP Interelement Correction Factors

LABORATORY _____ ICP Model Number _____

DATE _____

Analyte	Analyte Wavelength (nm)	Interelement Correction Factors for Al	Ca	Fe	Mg				
1. Antimony									
2. Arsenic									
3. Barium									
4. Beryllium									
5. Cadmium									
6. Chromium									
7. Cobalt									
8. Copper									
9. Lead									
10. Manganese									
11. Mercury									
12. Nickel									
13. Potassium									
14. Selenium									
15. Silver									
16. Sodium									
17. Thallium									
18. Vanadium									
19. Zinc									

COMMENTS: _____

Lab Manager _____

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Date September 1986

Form XII

ICP Interelement Correction Factors

LABORATORY _____ ICP Model Number _____

DATE _____

Analyte	Analyte Wavelength (nm)	Interelement Correction Factors for							
1. Antimony									
2. Arsenic									
3. Barium									
4. Beryllium									
5. Cadmium									
6. Chromium									
7. Cobalt									
8. Copper									
9. Lead									
10. Manganese									
11. Mercury									
12. Nickel									
13. Potassium									
14. Selenium									
15. Silver									
16. Sodium									
17. Thallium									
18. Vanadium									
19. Zinc									

COMMENTS: _____

Lab Manager _____

Revision 0
Date September 1986

Form XIII

ICP Linear Ranges

LAB NAME _____ ICP Model Number _____

DATE _____

Analyte	Integration Time (Seconds)	Concentration (ug/L)	Analyte	Integration Time (Seconds)	Concentration (ug/L)
1. Aluminum			13. Magnesium		
2. Antimony			14. Manganese		
3. Arsenic			15. Mercury		
4. Barium			16. Nickel		
5. Beryllium			17. Potassium		
6. Cadmium			18. Selenium		
7. Calcium			19. Silver		
8. Chromium			20. Sodium		
9. Cobalt			21. Thallium		
10. Copper			22. Vanadium		
11. Iron			23. Zinc		
12. Lead					

Footnotes: • Indicate elements not analyzed by ICP with the notation "NA".

COMMENTS: _____

_____

_____

_____

Lab Manager _____

Revision 0
Date September 1986

Organics Analysis Data Sheet
(Page 1)

Sample Number

Laboratory Name: _____ Case No: _____

Lab Sample ID No: _____ QC Report No: _____

Sample Matrix: _____

Data Release Authorized By: _____ Date Sample Received: _____

Volatile Compounds

Date Extracted/Prepared: _____

Date Analyzed: _____

Conc/Dil Factor: _____ pH _____

Percent Moisture: (Not Decanted) _____

CAS Number		ug/l or ug/Kg (Circle One)
74-87-3	Chloromethane	
74-83-9	Bromomethane	
75-01-4	Vinyl Chloride	
75-00-3	Chloroethane	
75-09-2	Methylene Chloride	
67-64-1	Acetone	
75-15-0	Carbon Disulfide	
75-35-4	1, 1-Dichloroethene	
75-34-3	1, 1-Dichloroethane	
156-60-5	Trans-1, 2-Dichloroethene	
67-66-3	Chloroform	
107-06-2	1, 2-Dichloroethane	
78-93-3	2-Butanone	
71-55-6	1, 1, 1-Trichloroethane	
56-23-5	Carbon Tetrachloride	
108-05-4	Vinyl Acetate	
75-27-4	Bromodichloromethane	

CAS Number		ug/l or ug/Kg (Circle One)
78-87-5	1, 2-Dichloropropane	
10061-02-6	Trans-1, 3-Dichloropropene	
79-01-6	Trichloroethene	
124-48-1	Dibromochloromethane	
79-00-5	1, 1, 2-Trichloroethane	
71-43-2	Benzene	
10061-01-5	cis-1, 3-Dichloropropene	
110-75-8	2-Chloroethylvinylether	
75-25-2	Bromoform	
108-10-1	4-Methyl-2-Pentanone	
591-78-6	2-Hexanone	
127-18-4	Tetrachloroethene	
79-34-5	1, 1, 2, 2-Tetrachloroethane	
108-88-3	Toluene	
108-90-7	Chlorobenzene	
100-41-4	Ethylbenzene	
100-42-5	Styrene	
	Total Xylenes	

Data Reporting Qualifiers

For reporting results to EPA, the following results qualifiers are used. Additional flags or footnotes explaining results are encouraged. However, the definition of each flag must be explicit.

Value If the result is a value greater than or equal to the detection limit, report the value

U Indicates compound was analyzed for but not detected. Report the minimum detection limit for the sample with the U (e.g., 10U) based on necessary concentration/dilution action. (This is not necessarily the instrument detection limit.) The footnote should read "U - Compound was analyzed for but not detected. The number is the minimum attainable detection limit for the sample."

J Indicates an estimated value. This flag is used either when estimating a concentration for tentatively identified compounds where a 1:1 response is assumed or when the mass spectral data indicated the presence of a compound that meets the identification criteria but the result is less than the specified detection limit but greater than zero (e.g., 10J). If limit of detection is 10 µg/l and a concentration of 3 µg/l is calculated, report as 3J.

C This flag applies to pesticide parameters where the identification has been confirmed by GC/MS. Single component pesticides ≥ 10 ng/ul in the final extract should be confirmed by GC/MS.

B This flag is used when the analyte is found in the blank as well as a sample. It indicates possible/probable blank contamination and warns the data user to take appropriate action.

Other Other specific flags and footnotes may be required to properly define the results. If used, they must be fully described and such description attached to the data summary report.

Form I

Revision 0
Date September 1986

Laboratory Name: _____

Case No: _____

Sample Number

Organics Analysis Data Sheet
(Page 2)

Semivolatile Compounds

GPC Cleanup ☐Yes ☐No

Date Extracted/Prepared: _____

Separatory Funnel Extraction ☐Yes

Date Analyzed: _____

Continuous Liquid - Liquid Extraction ☐Yes

Conc/Dil Factor: _____

Percent Moisture (Decanted) _____

CAS Number		ug/l or ug/Kg (Circle One)
108-95-2	Phenol	
111-44-4	bis(-2-Chloroethyl)Ether	
95-57-8	2-Chlorophenol	
541-73-1	1, 3-Dichlorobenzene	
106-46-7	1, 4-Dichlorobenzene	
100-51-6	Benzyl Alcohol	
95-50-1	1, 2-Dichlorobenzene	
95-48-7	2-Methylphenol	
39638-32-9	bis(2-chloroisopropyl)Ether	
106-44-5	4-Methylphenol	
621-64-7	N-Nitroso-Di-n-Propylamine	
67-72-1	Hexachloroethane	
98-95-3	Nitrobenzene	
78-59-1	Isophorone	
88-75-5	2-Nitrophenol	
105-67-9	2, 4-Dimethylphenol	
65-85-0	Benzoic Acid	
111-91-1	bis(-2-Chloroethoxy)Methane	
120-83-2	2, 4-Dichlorophenol	
120-82-1	1, 2, 4-Trichlorobenzene	
91-20-3	Naphthalene	
106-47-8	4-Chloroaniline	
87-68-3	Hexachlorobutadiene	
59-50-7	4-Chloro-3-Methylphenol	
91-57-6	2-Methylnaphthalene	
77-47-4	Hexachlorocyclopentadiene	
88-06-2	2, 4, 6-Trichlorophenol	
95-95-4	2, 4, 5-Trichlorophenol	
91-58-7	2-Chloronaphthalene	
88-74-4	2-Nitroaniline	
131-11-3	Dimethyl Phthalate	
208-96-8	Acenaphthylene	
99-09-2	3-Nitroaniline	

CAS Number		ug/l or ug/Kg (Circle One)
83-32-9	Acenaphthene	
51-28-5	2, 4-Dinitrophenol	
100-02-7	4-Nitrophenol	
132-64-9	Dibenzofuran	
121-14-2	2, 4-Dinitrotoluene	
606-20-2	2, 6-Dinitrotoluene	
84-66-2	Diethylphthalate	
7005-72-3	4-Chlorophenyl-phenylether	
86-73-7	Fluorene	
100-01-6	4-Nitroaniline	
534-52-1	4, 6-Dinitro-2-Methylphenol	
86-30-6	N-Nitrosodiphenylamine (1)	
101-55-3	4-Bromophenyl-phenylether	
118-74-1	Hexachlorobenzene	
87-86-5	Pentachlorophenol	
85-01-8	Phenanthrene	
120-12-7	Anthracene	
84-74-2	Di-n-Butylphthalate	
206-44-0	Fluoranthene	
129-00-0	Pyrene	
85-68-7	Butylbenzylphthalate	
91-94-1	3, 3'-Dichlorobenzidine	
56-55-3	Benzo(a)Anthracene	
117-81-7	bis(2-Ethylhexyl)Phthalate	
218-01-9	Chrysene	
117-84-0	Di-n-Octyl Phthalate	
205-99-2	Benzo(b)Fluoranthene	
207-08-9	Benzo(k)Fluoranthene	
50-32-8	Benzo(a)Pyrene	
193-39-5	Indeno(1, 2, 3-cd)Pyrene	
53-70-3	Dibenz(a, h)Anthracene	
191-24-2	Benzo(g, h, i)Perylene	

(1)-Cannot be separated from diphenylamine

Laboratory Name: _____

Case No: _____

Sample Number

Organics Analysis Data Sheet
(Page 3)

Pesticide/PCBs

GPC Cleanup ☐Yes ☐No

Date Extracted/Prepared: _____

Separatory Funnel Extraction ☐Yes

Date Analyzed: _____

Continuous Liquid - Liquid Extraction ☐Yes

Conc/Dil Factor: _____

Percent Moisture (decanted) _____

CAS Number		ug/l or ug/Kg (Circle One)
319-84-6	Alpha-BHC	
319-85-7	Beta-BHC	
319-86-8	Delta-BHC	
58-89-9	Gamma-BHC (Lindane)	
76-44-8	Heptachlor	
309-00-2	Aldrin	
1024-57-3	Heptachlor Epoxide	
959-98-8	Endosulfan I	
60-57-1	Dieldrin	
72-55-9	4, 4'-DDE	
72-20-8	Endrin	
33213-65-9	Endosulfan II	
72-54-8	4, 4'-DDD	
1031-07-8	Endosulfan Sulfate	
50-29-3	4, 4'-DDT	
72-43-5	Methoxychlor	
53494-70-5	Endrin Ketone	
57-74-9	Chlordane	
8001-35-2	Toxaphene	
12674-11-2	Aroclor-1016	
11104-28-2	Aroclor-1221	
11141-16-5	Aroclor-1232	
53469-21-9	Aroclor-1242	
12672-29-6	Aroclor-1248	
11097-69-1	Aroclor-1254	
11096-82-5	Aroclor-1260	

V_i = Volume of extract injected (ul)

V_s = Volume of water extracted (ml)

W_s = Weight of sample extracted (g)

V_t = Volume of total extract (ul)

V_s _____ or W_s _____ V_t _____ V_i _____

Laboratory Name: _____

Case No: _____

Sample Number

Organics Analysis Data Sheet

CAS Number	Compound Name	Fraction	RT or Scan Number	Estimated Concentration (ug/l or ug/kg)
1.				
2.				
3.				
4.				
5.				
6.				
7.				
8.				
9.				
10.				
11.				
12.				
13.				
14.				
15.				
16.				
17.				
18.				
19.				
20.				
21.				
22.				
23.				
24.				
25.				
26.				
27.				
28.				
29.				
30.				

Form 1, Part B

Revision 0
Date September 1986

WATER SURROGATE PERCENT RECOVERY SUMMARY

Case No. _____ **Laboratory Name** _____

	VOLATILE			SEMI-VOLATILE								PESTICIDE
SAMPLE NO.	TOLUENE-D8 (88-110)	BFB (86-115)	1,2 DICHLOROETHANE-D4 (76-114)	NITROBENZENE-D5 (35-114)	2-FLUOROBIPHENYL (43-116)	TERPHENYL-D14 (33-141)			PHENOL-D5 (10-94)	2-FLUOROPHENOL (21-100)	2,4,6 TRIBROMOPHENOL (10-123)	DIBUTYLCHLORENDATE (24-154)

VALUES ARE OUTSIDE OF REQUIRED QC LIMITS

Volatiles: _____ out of _____ ; outside of QC limits
Semi-Volatiles: _____ out of _____ ; outside of QC limits
Pesticides: _____ out of _____ ; outside of QC limits

Comments: _____

FORM II

Revision 0
Date September 1986

SOIL SURROGATE PERCENT RECOVERY SUMMARY

Case No. _____ Laboratory Name _____

	VOLATILE			SEMI-VOLATILE							PESTICIDE
SAMPLE NO.	TOLUENE-D8 (81-117)	BFB (74-121)	1,2 DICHLOROETHANE-D4 (70-121)	NITROBENZENE-D5 (23-120)	2-FLUOROBIPHENYL (30-115)	TERPHENYL-D14 (18-137)			PHENOL-D5 (24-113)	2-FLUOROPHENOL (25-121)	2,4,6 TRIBROMOPHENOL (19-122)	DIBUTYLCHLORENDATE (20-150)

VALUES ARE OUTSIDE OF REQUIRED QC LIMITS

Volatiles: _____ out of _____ ; outside of QC limits
Semi-Volatiles: _____ out of _____ ; outside of QC limits
Pesticides: _____ out of _____ ; outside of QC limits

Comments: _____

FORM II

Revision 0
Date September 1986

WATER MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Case No. _____ **Laboratory Name** _____

FRACTION	COMPOUND	CONC. SPIKE ADDED (ug/L)	SAMPLE RESULT	CONC. MS	% REC	CONC. MSD	% REC	RPD	QC LIMITS RPD	QC LIMITS RECOVERY
VOA	1,1-Dichloroethene								14	61-145
	Trichloroethene								14	71-120
SAMPLE NO.	Chlorobenzene								13	75-130
	Toluene								13	76-125
_____	Benzene								11	76-127
B/N	1,2,4-Trichlorobenzene								28	39-98
	Acenaphthene								31	46-118
	2,4 Dinitrotoluene								38	24-96
SAMPLE NO.	Di-n-Butylphthalate								40	11-117
	Pyrene								31	26-127
	N-Nitroso-Di-n-Propylamine								38	41-116
_____	1,4-Dichlorobenzene								28	36-97
ACID	Pentachlorophenol								50	9-103
	Phenol								42	12-89
	2-Chlorophenol								40	27-123
SAMPLE NO.	4-Chloro-3-Methylphenol								42	23-97
_____	4-Nitrophenol								50	10-80
PEST	Lindane								15	56-123
	Heptachlor								20	40-131
	Aldrin								22	40-120
SAMPLE NO.	Dieldrin								18	52-126
	Endrin								21	56-121
_____	4,4'-DDT								27	38-127

ADVISORY LIMITS

RPD: VOAs _____ out of _____; outside QC limits
B/N _____ out of _____; outside QC limits
ACID _____ out of _____; outside QC limits
PEST _____ out of _____; outside QC limits

RECOVERY: VOAs _____ out of _____; outside QC limits
B/N _____ out of _____; outside QC limits
ACID _____ out of _____; outside QC limits
PEST _____ out of _____; outside QC limits

Comments: _____

_____

_____

_____

_____

FORM III

Revision 0
Date September 1986

SOIL MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Case No. _____ **Laboratory Name** _____

FRACTION	COMPOUND	CONC. SPIKE ADDED (ug/Kg)	SAMPLE RESULT	CONC. MS	% REC	CONC. MSD	% REC	RPD	QC LIMITS RPD	QC LIMITS RECOVERY
VOA	1,1-Dicholorethene								22	59-172
	Trichloroethene								24	62-137
SAMPLE NO.	Chlorobenzene								21	60-133
	Toluene								21	59-139
_____	Benzene								21	66-142
B/N	1,2,4-Trichlorobenzene								23	38-107
	Acenaphthene								19	31-137
	2,4 Dinitrotoluene								47	28-89
SAMPLE NO.	Di-n-Butylphthalate								47	29-135
	Pyrene								36	35-142
	N-Nitrosodi-n-Propylamine								38	41-126
_____	1,4-Dichlorobenzene								27	28-104
ACID	Pentachlorophenol								47	17-109
	Phenol								35	26-90
	2-Chlorophenol								50	25-102
SAMPLE NO.	4-Chloro-3-Methylphenol								33	26-103
_____	4-Nitrophenol								50	11-114
PEST	Lindane								50	46-127
	Heptachlor								31	35-130
	Aldrin								43	34-132
SAMPLE NO.	Dieldrin								38	31-134
	Endrin								45	42-139
_____	4,4'-DDT								50	23-134

ADVISORY LIMITS

RPD: VOAs ____ out of ____; outside QC limits
B/N ____ out of ____; outside QC limits
ACID ____ out of ____; outside QC limits
PEST ____ out of ____; outside QC limits

RECOVERY: VOAs ____ out of ____; outside QC limits
B/N ____ out of ____; outside QC limits
ACID ____ out of ____; outside QC limits
PEST ____ out of ____; outside QC limits

Comments: _____

FORM III

Revision 0
Date September 1986

METHOD BLANK SUMMARY

Case No. _____ Laboratory Name _____

FILE ID	DATE OF ANALYSIS	FRACTION	MATRIX	CONC. LEVEL	INST. ID	CAS NUMBER	COMPOUND (HSL,TIC OR UNKNOWN)	CONC.	UNITS	CRDL

Comments:

GC/MS TUNING AND MASS CALIBRATION
Bromofluorobenzene (BFB)

Case No. _____ **Laboratory Name** _____

Instrument ID _____ Date _____ Time _____

Data Release Authorized By: _____

m/e	ION ABUNDANCE CRITERIA	%RELATIVE ABUNDANCE
50	15.0 - 40.0% of the base peak	
75	30.0 - 60.0% of the base peak	
95	Base peak, 100% relative abundance	
96	5.0 - 9.0% of the base peak	
173	Less than 1.0% of the base peak	
174	Greater than 50.0% of the base peak	
175	5.0 - 9.0% of mass 174	( )[1]
176	Greater than 95.0%, but less than 101.0% of mass 174	( )[1]
177	5.0 - 9.0% of mass 176	( )[2]

THIS PERFORMANCE TUNE APPLIES TO THE FOLLOWING SAMPLES, BLANKS AND STANDARDS.

[1]Value in parenthesis is % mass 174.
[2]Value in parenthesis is % mass 176.

SAMPLE ID	LAB ID	DATE OF ANALYSIS	TIME OF ANALYSIS

FORM V

Revision 0
Date September 1986

GC/MS TUNING AND MASS CALIBRATION
Decafluorotriphenylphosphine (DFTPP)

Case No. _____ **Laboratory Name** _____

Instrument ID _____ Date _____ Time _____

Data Release Authorized By: _____

m/e	ION ABUNDANCE CRITERIA	%RELATIVE ABUNDANCE
51	30.0 - 60.0% of mass 198	
68	less than 2.0% of mass 69	( )[1]
69	mass 69 relative abundance	
70	less than 2.0% of mass 69	( )[1]
127	40.0 - 60.0% of mass 198	
197	less than 1.0% of mass 198	
198	base peak, 100% relative abundance	
199	5.0 - 9.0% of mass 198	
275	10.0 - 30.0% of mass 198	
365	greater than 1.00% of mass 198	
441	present, but less than mass 443	
442	greater than 40.0% of mass 198	
443	17.0 - 23.0% of mass 442	( )[2]

THIS PERFORMANCE TUNE APPLIES TO THE FOLLOWING SAMPLES, BLANKS AND STANDARDS.

[1] Value in parenthesis is % mass 69.
[2] Value in parenthesis is % mass 442.

SAMPLE ID	LAB ID	DATE OF ANALYSIS	TIME OF ANALYSIS

FORM V

Revision 0
Date September 1986

Initial Calibration Data
Volatile HSL Compounds

Case No: _____ Instrument I D: _____

Laboratory Name _____ Calibration Date: _____

Minimum $\overline{RF}$ for SPCC is 0.300 (0.25 for Bromoform)

Maximum % RSD for CCC is 30%

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{100}	RF_{150}	RF_{200}	$\overline{RF}$	% RSD	CCC* SPCC**
Chloromethane								**
Bromomethane								
Vinyl Chloride								*
Chloroethane								
Methylene Chloride								
Acetone								
Carbon Disulfide								
1, 1-Dichloroethene								*
1, 1-Dichloroethane								**
Trans-1, 2-Dichloroethene								
Chloroform								*
1, 2-Dichloroethane								
2-Butanone								
1, 1, 1-Trichloroethane								
Carbon Tetrachloride								
Vinyl Acetate								
Bromodichloromethane								
1, 2-Dichloropropane								*
Trans-1, 3-Dichloropropene								
Trichloroethene								
Dibromochloromethane								
1, 1, 2-Trichloroethane								
Benzene								
cis-1, 3-Dichloropropene								
2-Chloroethylvinylether								
Bromoform								**
4-Methyl-2-Pentanone								
2-Hexanone								
Tetrachloroethene								
1, 1, 2, 2-Tetrachloroethane								**
Toluene								*
Chlorobenzene								**
Ethylbenzene								*
Styrene								
Total Xylenes								

RF -Response Factor (subscript is the amount of ug/L)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation

CCC -Calibration Check Compounds (*)
SPCC -System Performance Check Compounds (**)

Form VI

Revision 0
Date September 1986

Initial Calibration Data
Volatile HSL Compounds

Case No: ______________ Instrument I D: ______________________

Laboratory Name ______________________ Calibration Date: ______________________

Minimum $\overline{RF}$ for SPCC is **0.300** (0.25 for Bromoform) Maximum % RSD for CCC is **30%**

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{100}	RF_{150}	RF_{200}	$\overline{RF}$	% RSD	CCC• SPCC••

RF -Response Factor (subscript is the amount of ug/L)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation

CCC -Calibration Check Compounds (•)
SPCC -System Performance Check Compounds (••)

Form VI

Initial Calibration Data
Semivolatile HSL Compounds
(Page 1)

Case No: _____ Instrument ID: _____

Laboratory Name _____ Calibration Date: _____

Minimum $\overline{RF}$ for SPCC is 0.050 Maximum % RSD for CCC is 30%

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{80}	RF_{120}	RF_{160}	$\overline{RF}$	%RSD	CCC* SPCC**
Phenol								*
bis(-2-Chloroethyl)Ether								
2-Chlorophenol								
1, 3-Dichlorobenzene								
1, 4-Dichlorobenzene								*
Benzyl Alcohol								
1, 2-Dichlorobenzene								
2-Methylphenol								
bis(2-chloroisopropyl)Ether								
4-Methylphenol								
N-Nitroso-Di-n-Propylamine								* *
Hexachloroethane								
Nitrobenzene								
Isophorone								
2-Nitrophenol								*
2, 4-Dimethylphenol								
Benzoic Acid	†							
bis(-2-Chloroethoxy)Methane								
2, 4-Dichlorophenol								*
1, 2, 4-Trichlorobenzene								
Naphthalene								
4-Chloroaniline								
Hexachlorobutadiene								*
4-Chloro-3-Methylphenol								*
2-Methylnaphthalene								
Hexachlorocyclopentadiene								* *
2, 4, 6-Trichlorophenol								*
2, 4, 5-Trichlorophenol	†							
2-Chloronaphthalene								
2-Nitroaniline	†							
Dimethyl Phthalate								
Acenaphthylene								
3-Nitroaniline	†							
Acenaphthene								*
2, 4-Dinitrophenol	†							* *
4-Nitrophenol	†							* *
Dibenzofuran								

Response Factor (subscript is the amount of nanograms)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation
CCC -Calibration Check Compounds (*)
SPCC -System Performance Check Compounds (**)
† -Not detectable at 20 ng

Form VI

Revision 0
Date September 1986

Initial Calibration Data
Semivolatile HSL Compounds
(Page 2)

Case No: _____ Instrument ID: _____

Laboratory Name _____ Calibration Date: _____

Minimum $\overline{RF}$ for SPCC is 0.050 Maximum % RSD for CCC is 30%

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{80}	RF_{120}	RF_{160}	$\overline{RF}$	% RSD	CCC* SPCC**
2, 4-Dinitrotoluene								
2, 6-Dinitrotoluene								
Diethylphthalate								
4-Chlorophenyl-phenylether								
Fluorene								
4-Nitroaniline	†							
4, 6-Dinitro-2-Methylphenol	†							
N-Nitrosodiphenylamine (1)								*
4-Bromophenyl-phenylether								
Hexachlorobenzene								
Pentachlorophenol	†							*
Phenanthrene								
Anthracene								
Di-N-Butylphthalate								
Fluoranthene								*
Pyrene								
Butylbenzylphthalate								
3, 3'-Dichlorobenzidine								
Benzo(a)Anthracene								
bis(2-Ethylhexyl)Phthalate								
Chrysene								
Di-n-Octyl Phthalate								*
Benzo(b)Fluoranthene								
Benzo(k)Fluoranthene								
Benzo(a)Pyrene								*
Indeno(1, 2, 3-cd)Pyrene								
Dibenz(a, h)Anthracene								
Benzo(g, h, i)Perylene								

Response Factor (subscript is the amount of nanograms)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation
CCC -Calibration Check Compounds (•)
SPCC -System Performance Check Compounds (••)
† - Not detectable at 20 ng
(1) -Cannot be separated from diphenylamine

Form VI

Revision 0
Date September 1986

Initial Calibration Data
Semivolatile HSL Compounds
(Page 1)

Case No: ____________ Instrument ID: ____________________

Laboratory Name ____________________ Calibration Date: ____________________

Minimum $\overline{RF}$ for SPCC is **0.050** Maximum % RSD for CCC is **30%**

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{80}	RF_{120}	RF_{160}	$\overline{RF}$	% RSD	CCC• SPCC••

Response Factor (subscript is the amount of nanograms)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation
CCC -Calibration Check Compounds (•)
SPCC -System Performance Check Compounds (••)
† -Not detectable at 20 ng

Form VI

Continuing Calibration Check
Volatile HSL Compounds

Case No: _____ Calibration Date: _____

Laboratory Name _____ Time: _____

Contract No: _____ **Laboratory ID:** _____

Instrument ID: _____ Initial Calibration Date: _____

Minimum RF for SPCC is 0.300 (0.25 for Bromoform) Maximum %D for CCC is 25%

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC
Chloromethane					**
Bromomethane					
Vinyl Chloride				*	
Chloroethane					
Methylene Chloride					
Acetone					
Carbon Disulfide					
1, 1-Dichloroethene				*	
1, 1-Dichloroethane					**
Trans-1, 2-Dichloroethene					
Chloroform				*	
1, 2-Dichloroethane					
2-Butanone					
1, 1, 1-Trichloroethane					
Carbon Tetrachloride					
Vinyl Acetate					
Bromodichloromethane					
1, 2-Dichloropropane				*	
Trans-1, 3-Dichloropropene					
Trichloroethene					
Dibromochloromethane					
1, 1, 2-Trichloroethane					
Benzene					
cis-1, 3-Dichloropropene					
2-Chloroethylvinylether					
Bromoform					**
4-Methyl-2-Pentanone					
2-Hexanone					
Tetrachloroethene					
1, 1, 2, 2-Tetrachloroethane					**
Toluene		*		*	
Chlorobenzene					**
Ethylbenzene				*	
Styrene					
Total Xylenes					

RF_{50} -Response Factor from daily standard file at 50 ug/l
RF -Average Response Factor from initial calibration Form VI

%D -Percent Difference
CCC -Calibration Check Compounds (*)
SPCC -System Performance Check Compounds (**)

Form VII

Revision 0
Date September 1986

Continuing Calibration Check
Volatile HSL Compounds

Case No: ____________ Calibration Date: ____________

Laboratory Name ____________ Time: ____________

Contract No: ____________ Laboratory ID: ____________

Instrument ID: ____________ Initial Calibration Date: ____________

Minimum RF for SPCC is 0.300 (0.25 for Bromoform)

Maximum %D for CCC is **25%**

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC

RF_{50} - Response Factor from daily standard file at 50 ug/l

$\overline{RF}$ - Average Response Factor from initial calibration Form VI

%D - Percent Difference

CCC - Calibration Check Compounds (•)

SPCC - System Performance Check Compounds (••)

Form VII

Continuing Calibration Check
Semivolatile HSL Compounds
(Page 1)

Case No: _____ Calibration Date: _____

Laboratory Name _____ Time: _____

Laboratory ID: _____

Instrument ID: _____ Initial Calibration Date: _____

Minimum RF for SPCC is 0.050 Maximum %D for CCC is 25%

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC
Phenol				*	
bis(-2-Chloroethyl)Ether					
2-Chlorophenol					
1, 3-Dichlorobenzene					
1, 4-Dichlorobenzene				*	
Benzyl Alcohol					
1, 2-Dichlorobenzene					
2-Methylphenol					
bis(2-chloroisopropyl)Ether					
4-Methylphenol					
N-Nitroso-Di-n-Propylamine					* *
Hexachloroethane					
Nitrobenzene					
Isophorone					
2-Nitrophenol				*	
2, 4-Dimethylphenol					
Benzoic Acid †					
bis(-2-Chloroethoxy)Methane					
2, 4-Dichlorophenol				*	
1, 2, 4-Trichlorobenzene					
Naphthalene					
4-Chloroaniline					
Hexachlorobutadiene				*	
4-Chloro-3-Methylphenol				*	
2-Methylnaphthalene					
Hexachlorocyclopentadiene					* *
2, 4, 6-Trichlorophenol				*	
2, 4, 5-Trichlorophenol †					
2-Chloronaphthalene					
2-Nitroaniline †					
Dimethyl Phthalate					
Acenaphthylene					
3-Nitroaniline †					
Acenaphthene				*	
2, 4-Dinitrophenol †					* *
4-Nitrophenol †					* *
Dibenzofuran					

RF_{50} -Response Factor from daily standard file at concentration indicated (50 total nanograms)

$\overline{RF}$ -Average Response Factor from initial calibration Form VI

†-Due to low response, analyze at 80 total nanograms

%D -Percent Difference

CCC -Calibration Check Compounds (*)

SPCC -System Performance Check Compounds (**)

Continuing Calibration Check
Semivolatile HSL Compounds
(Page 2)

Case No: _____ Calibration Date: _____

Laboratory Name _____ Time: _____

Laboratory ID: _____

Instrument ID: _____ Initial Calibration Date: _____

Minimum RF for SPCC is 0.050 Maximum %D for CCC is 25%

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC
2, 4-Dinitrotoluene					
2, 6-Dinitrotoluene					
Diethylphthalate					
4-Chlorophenyl-phenylether					
Fluorene					
4-Nitroaniline †					
4, 6-Dinitro-2-Methylphenol †					
N-Nitrosodiphenylamine (1)				*	
4-Bromophenyl-phenylether					
Hexachlorobenzene					
Pentachlorophenol †				*	
Phenanthrene					
Anthracene					
Di-N-Butylphthalate					
Fluoranthene				*	
Pyrene					
Butylbenzylphthalate					
3, 3'-Dichlorobenzidine					
Benzo(a)Anthracene					
bis(2-Ethylhexyl)Phthalate					
Chrysene					
Di-n-Octyl Phthalate				*	
Benzo(b)Fluoranthene					
Benzo(k)Fluoranthene					
Benzo(a)Pyrene				*	
Indeno(1, 2, 3-cd)Pyrene					
Dibenz(a, h)Anthracene					
Benzo(g, h, i)Perylene					

RF_{50} - Response Factor from daily standard file at concentration indicated (50 total nanograms)

$\overline{RF}$ - Average Response Factor from initial calibration Form VI

%D - Percent Difference

† - Due to low response, analyze at 80 total nanograms

CCC - Calibration Check Compounds (*)

SPCC - System Performance Check Compounds (**)

(1) - Cannot be separated from diphenylamine

Form VII

Revision 0
Date September 1986

Continuing Calibration Check
Semivolatile HSL Compounds
(Page 1)

Case No: ______________

Laboratory Name ______________________________

Instrument ID: ______________________________

Calibration Date: ______________________________

Time: ______________________________

Laboratory ID: ______________________________

Initial Calibration Date: ______________________________

Minimum RF for SPCC is 0.050   Maximum %D for CCC is 25%

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC

RF_{50} -Response Factor from daily standard file at concentration indicated (50 total nanograms)

$\overline{RF}$ -Average Response Factor from initial calibration Form VI

† -Due to low response, analyze at 80 total nanograms

%D -Percent Difference

CCC -Calibration Check Compounds (•)

SPCC System Performance Check Compounds (••)

Form VII

Pesticide Evaluation Standards Summary
(Page 1)

Case No: _____ **Laboratory Name**: _____

GC Column: _____

Date of Analysis: _____ Instrument ID: _____

Evaluation Check for Linearity

Laboratory ID				
Pesticide	Calibration Factor Eval. Mix A	Calibration Factor Eval. Mix B	Calibration Factor Eval. Mix C	% RSD (≤10%)
Aldrin				
Endrin				
4,4'- DDT(1)				
Dibutyl Chlorendate				

Evaluation Check for 4,4'- DDT/Endrin Breakdown
(percent breakdown expressed as total degradation)

	Laboratory I.D.	Time of Analysis	Endrin	4,4'- DDT	Combined(2)
Eval Mix B 72 Hour					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					

(1) See Exhibit E, Section 7.5.4
(2) See Exhibit E, Section 7.3.1.2.2.1

Pesticide Evaluation Standards Summary
(Page 2)

Evaluation of Retention Time Shift for Dibutyl Chlorendate

Report all standards, blanks and samples

Sample No	Lab I.D.	Time of Analysis	Percent Diff.	SMO Sample No.	Lab I.D.	Time of Analysis	Percent Diff.

Form VIII (Continued)

RCRA
4/86

PESTICIDE/PCB STANDARDS SUMMARY

Case No. _____ Laboratory Name _____

GC Column _____ GC Instrument ID _____

	DATE OF ANALYSIS _____ TIME OF ANALYSIS _____ LABORATORY ID _____				DATE OF ANALYSIS _____ TIME OF ANALYSIS _____ LABORATORY ID _____			
COMPOUND	RT	RETENTION TIME WINDOW	CALIBRATION FACTOR	CONF. OR QUANT.	RT	CALIBRATION FACTOR	CONF. OR QUANT.	PERCENT DIFF.**
alpha-BHC								
beta-BHC								
delta-BHC								
gamma-BHC								
Heptachlor								
Aldrin								
Heptachlor Epoxide								
Endosulfan I								
Dieldrin								
4,4'-DDE								
Endrin								
Endosulfan II								
4,4'-DDD								
Endrin Aldehyde								
Endosulfan Sulfate								
4,4'-DDT								
Methoxychlor								
Endrin Ketone								
Tech. Chlordane								
alpha-Chlordane								
gamma-Chlordane								
Toxaphene								
Aroclor - 1016								
Aroclor - 1221								
Aroclor - 1232								
Aroclor - 124.								
Aroclor - 1248								
Aroclor - 1254								
Aroclor - 1260								

** CONF. = CONFIRMATION (<20% DIFFERENCE)
QUANT. = QUANTITATION (<15% DIFFERENCE)

FORM IX

Revision 0
Date September 1986

Pesticide/PCB Identification

Case No. ____________________ Laboratory Name ____________________

SAMPLE ID	PRIMARY COLUMN	PESTICIDE/ PCB	RT OF TENTATIVE ID	RT WINDOW OF APPROPRIATE STANDARD	CONFIRMATION COLUMN	RT ON CONFIRMATORY COLUMN	RT WINDOW OF APPROPRIATE STANDARD	GC/MS CONFIRMED (Y or N)

FORM X

CHAPTER FOUR

ORGANIC ANALYTES

4.1 SAMPLING CONSIDERATIONS

4.1.1 Introduction

Following the initial and critical step of designing a sampling plan (Chapter Nine) is the implementation of that plan such that a representative sample of the solid waste is collected. Once the sample has been collected it must be stored and preserved to maintain the chemical and physical properties that it possessed at the time of collection. The sample type, type of containers and their preparation, possible forms of contamination, and preservation methods are all items which must be thoroughly examined in order to maintain the integrity of the samples. This section highlights considerations which must be addressed in order to maintain a sample's integrity and representativeness.

4.1.2 Sample Handling and Preservation

This section deals separately with volatile and semivolatile organics. Refer to Chapter Two (Table 2-16) and Table 4-1 of this Section for recommended sample containers, sample preservation, and sample holding times.

Volatile Organics

Standard 40-mL glass screw-cap VOA vials with Teflon-faced silicone septum may be used for both liquid and solid matrices. The vials and septum should be soap and water washed and rinsed with distilled deionized water. After thoroughly cleaning the vials and septum, they should be placed in a muffle furnace and dried at 105°C for approximately one hour. (Note: Do not heat the septum for extended periods of time, i.e., more than one hr, because the silicone begins to slowly degrade at 105°C).

When collecting the samples, liquids and solids should be introduced into the vials gently to reduce agitation which might drive off volatile compounds. Liquid samples should be poured into the vial without introducing any air bubbles within the vial as it is being filled. Should bubbling occur as a result of violent pouring, the sample must be poured out and the vial refilled. Each VOA vial should be filled until there is a meniscus over the lip of the vial. The screw-top lid with the septum (Teflon side toward the sample) should then be tightened onto the vial. After tightening the lid, the vial should be inverted and tapped to check for air bubbles. If there are any air bubbles present the sample must be retaken. Two VOA vials should be filled per sample location.

VOA vials for samples with solid or semi-solid (sludges) matrices should be completely filled as best as possible. The vials should be tapped slightly as they are filled to try and eliminate as much free air space as possible. Two vials should also be filled per sample location.

VOA vials should be filled and labeled immediately at the point at which the sample is collected. They should NOT be filled near a running motor or any type of exhaust system because discharged fumes and vapors may contaminate the samples. The two vials from each sampling locations should then be sealed in separate plastic bags to prevent cross-contamination between samples particularly if the sampled waste is suspected of containing high levels of volatile organics. (Activated carbon may also be included in the bags to prevent cross-contamination from highly contaminated samples). VOA samples may also be contaminated by diffusion of volatile organics through the septum during shipment and storage. To monitor possible contamination, a trip blank prepared from distilled deionized water should be carried throughout the sampling, storage, and shipping process.

Semivolatile Organics (This includes Pesticides and Herbicides.)

Containers used to collect samples for the determination of semivolatile organic compounds should be soap and water washed followed by methanol (or isopropanol) rinsing (see Section 4.1.4 for specific instructions on glassware cleaning). The sample containers should be of glass or Teflon and have screw-top covers with Teflon liners. In situations where Teflon is not available, solvent-rinsed aluminum foil may be used as a liner. Highly acidic or basic samples may react with the aluminum foil, causing eventual contamination of the sample. Plastic containers or lids may NOT be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic. Sample containers should be filled with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus causing contamination. Samples should not be collected or stored in the presence of exhaust fumes. If the sample comes in contact with the sampler (e.g., if an automatic sampler is used), run reagent water through the sampler and use as a field blank.

4.1.3 Safety

Safety should always be the primary consideration in the collection of samples. A thorough understanding of the waste production process as well as all of the potential hazards making up the waste should be investigated whenever possible. The site should be visually evaluated just prior to sampling to determine additional safety measures. Minimum protection of gloves and safety glasses should be worn to prevent sample contact with the skin and eyes. A respirator should be worn even when working outdoors if organic vapors are present. More hazardous sampling missions may require the use of supplied air and special clothing.

4.1.4 Cleaning of Glassware

In the analysis of samples containing components in the parts per billion range, the preparation of scrupulously clean glassware is mandatory. Failure to do so can lead to a myriad of problems in the interpretation of the final chromatograms due to the presence of extraneous peaks resulting from contamination. Particular care must be taken with glassware such as Soxhlet extractors, Kuderna-Danish evaporative concentrators, sampling-train

components, or any other glassware coming in contact with an extract that will be evaporated to a lesser volume. The process of concentrating the compounds of interest in this operation may similarly concentrate the contamination substance, which may seriously distort the results.

The basic cleaning steps are:

1. Removal of surface residuals immediately after use;

2. Hot soak to loosen and flotate most particulate material;

3. Hot-water rinse to flush away flotated particulates;

4. Soak with an oxidizing agent to destroy traces of organic compounds;

5. Hot-water rinse to flush away materials loosened by the deep penetrant soak;

6. Distilled-water rinse to remove metallic deposits from the tap water;

7. Methanol rinse to flush off any final traces of organic materials and remove the water; and

8. Flushing the item immediately before use with some of the same solvent that will be used in the analysis.

Each of these eight fundamental steps will be discussed in the order in which they appear above.

1. As soon possible after glassware (i.e., beakers, pipets, flasks, or bottles) has come in contact with sample or standards, the glassware should be methanol-flushed before it is placed in the hot detergent soak. If this is not done, the soak bath may serve to contaminate <u>all other</u> glassware placed therein.

2. The hot soak consists of a bath of a suitable detergent in water of 50°C or higher. The detergent -- powder or liquid -- should be entirely synthetic and not a fatty acid base. There are very few areas of the country where the water hardness is sufficiently low to avoid the formation of some hard-water scum resulting from the reaction between calcium and magnesium salts with a fatty acid soap. This hard-water scum or curd would have an affinity particularly for many chlorinated compounds and, being almost wholly water-insoluble, would deposit on all glassware in the bath in a thin film.

   There are many suitable detergents on the wholesale and retail market. Most of the common liquid dishwashing detergents sold at retail are satisfactory but are more expensive than other comparable products sold industrially. Alconox, in powder or tablet form, is manufactured by Alconox, Inc., New York, and is marketed by a number of laboratory supply firms. Sparkleen, another powdered product, is distributed by Fisher Scientific Company.

3. No comments required.

4. The most common and highly effective oxidizing agent for removal of traces of organic compounds is the traditional chromic acid solution made up of H_2SO_4 and potassium or sodium dichromate. For maximum efficiency, the soak solution should be hot (40-50°C). Safety precautions must be rigidly observed in the handling of this solution. Prescribed safety gear should include safety goggles, rubber gloves, and apron. The bench area where this operation is conducted should be covered with fluorocarbon sheeting because spattering will disintegrate any unprotected surfaces.

   The potential hazards of using chromic sulfuric acid mixture are great and have been well publicized. There are now commercially available substitutes that possess the advantage of safety in handling. These are biodegradable concentrates with a claimed cleaning strength equal to the chromic acid solution. They are alkaline, equivalent to ca. 0.1 N NaOH upon dilution, and are claimed to remove dried blood, silicone greases, distillation residues, insoluble organic residues, etc. They are further claimed to remove radioactive traces and will not attack glass or exert a corrosive effect on skin or clothing. One such product is "Chem Solv 2157," manufactured by Mallinckrodt and available through laboratory supply firms. Another comparable product is "Detex," a product of Borer-Chemie, Solothurn, Switzerland.

5, 6, and 7. No comments required.

8. There is always a possibility that between the time of washing and the next use, the glassware could pick up some contamination from either the air or direct contact. To ensure against this, it is good practice to flush the item immediately before use with some of the same solvent that will be used in the analysis.

The drying and storage of the cleaned glassware is of critical importance to prevent the beneficial effects of the scrupulous cleaning from being nullified. Pegboard drying is not recommended because contaminants can be introduced to the interior of the cleaned vessels. Neoprene-coated metal racks are suitable for such items as beakers, flasks, chromatographic tubes, and any glassware then can be inverted and suspended to dry. Small articles such as stirring rods, glass stoppers, and bottle caps can be wrapped in aluminum foil and oven-dried a short time if oven space is available. Under no circumstances should such small items be left in the open without protective covering. The dust cloud raised by the daily sweeping of the laboratory floor can most effectively recontaminate the clean glassware.

As an alternative to air drying, the glassware can be heated to a minimum of 300°C to vaporize any organics.

TABLE 4-1. RECOMMENDED SAMPLE CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

Parameter	Container	Preservative	Holding Time
Volatile Organics			
Concentrated Waste Samples	8-oz. widemouth glass with Teflon liner	None	14 days
Liquid Samples			
No Residual Chlorine Present	2 40-mL vials with Teflon lined septum caps	4 drops conc. HCl, Cool, 4°C	14 days
Residual Chlorine Present	2 40-mL vials with Teflon lined septum caps	Collect sample in a 4 oz. soil VOA container which has been pre-preserved with 4 drops of 10% sodium thiosulfate. Gently mix sample and transfer to a 40-mL VOA vial that has been pre-preserved with 4 drops conc. HCl, Cool to 4°C	14 days
Acrolein and Acrylonitrile	2 40-mL vials with Teflon lined septum caps	Adjust to pH 4-5, Cool, 4°C	14 days
Soil/Sediments and Sludges	4-oz (120-mL) widemouth glass with Teflon liner	Cool, 4°C	14 days

TABLE 4-1. Continued

Parameter	Container	Preservative	Holding Time
Semivolatile Organics			
Concentrated Waste Samples	8-oz. widemouth glass with Teflon liner	None	14 days
Liquid Samples			
No Residual Chlorine Present	1-gal. or 2 1/2-gal. amber glass with Teflon liner	Cool, 4°C	Samples must be extracted within 7 days and extracts analyzed within 40 days
Residual Chlorine Present	1-gal. or 2 1/2-gal. amber glass with Teflon liner	Add 3 mL 10% sodium thiosulfate per gallon, Cool, 4°C	Samples must be extracted within 7 days and extracts analyzed within 40 days
Soil/Sediments and Sludges	8-oz. widemouth glass with Teflon liner	Cool, 4°C	14 days

4.2 SAMPLE PREPARATION METHODS

4.2.1 EXTRACTIONS AND PREPARATIONS

METHOD 3500

ORGANIC EXTRACTION AND SAMPLE PREPARATION

1.0 SCOPE AND APPLICATION

1.1 The 3500 Methods are procedures for quantitatively extracting nonvolatile and semivolatile organic compounds from various sample matrices. Cleanup and/or analysis of the resultant extracts are described in Chapter Four, Sections 4.2.2 and 4.3, respectively.

1.2 Method 3580 describes a solvent dilution technique that may be used on non-aqueous nonvolatile and semivolatile organic samples prior to cleanup and/or analysis.

1.3 The 5000 Methods are procedures for preparing samples containing volatile organic compounds for quantitative analysis.

1.4 Refer to the specific method of interest for further details.

2.0 SUMMARY OF METHOD

2.1 3500 Methods: A sample of a known volume or weight is solvent extracted. The resultant extract is dried and then concentrated in a Kuderna-Danish apparatus. Other concentration devices or techniques may be used in place of the Kuderna-Danish concentrator if the quality control requirements of the determinative methods are met (Method 8000, Section 8.0).

2.2 5000 Methods: Refer to the specific method of interest.

3.0 INTERFERENCES

3.1 Samples requiring analysis for volatile organic compounds, can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.2 Solvents, reagent, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Refer to Chapter One for specific guidance on quality control procedures.

3.3 Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary. Refer to Method 3600 for guidance on cleanup procedures.

3.4 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

3.5 Glassware contamination resulting in analyte degradation: Soap residue on glassware may cause degradation of certain analytes. Specifically, aldrin, heptachlor, and most organophosphorous pesticides will degrade in this situation. This problem is especially pronounced with glassware that may be difficult to rinse (e.g., 500-mL K-D flask). These items should be hand-rinsed very carefully to avoid this problem.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific method of interest for a description of the apparatus and materials needed.

5.0 REAGENTS

5.1 Refer to the specific method of interest for a description of the solvents needed.

5.2 Stock standards: Stock solutions may be prepared from pure standard materials or purchased as certified solutions.

5.2.1 **Purgeable stock standards:** Prepare stock standards in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood.

5.2.1.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.2.1.2 Using a 100-uL syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.2.1.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (ug/uL) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.1.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.2.1.5 All standards must be replaced after 1 month, or sooner if comparison with check standards indicates a problem.

5.2.2 **Semivolatile stock standards:** Base/neutral and acid stock standards are prepared in methanol. Organochlorine pesticide standards are prepared in acetone.

5.2.2.1 Stock standard solutions should be stored in Teflon-sealed containers at 4°C. The solutions should be checked frequently for stability. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicate a problem.

5.3 Surrogate standards: A surrogate standard (i.e., a chemically inert compound not expected to occur in an environmental sample) should be added to each sample, blank, and matrix spike sample just prior to extraction or processing. The recovery of the surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within the acceptance limits. Recommended surrogates for different analyte groups follow; however, these compounds, or others that better correspond to the analyte group, may be used for other analyte groups as well. Normally three or more standards are added for each analyte group.

5.3.1 **Base/neutral and acid surrogate spiking solutions:** The following are recommended surrogate standards.

Base/neutral	Acid
2-Fluorobiphenyl	2-Fluorophenol
Nitrobenzene-d_5	2,4,6-Tribromophenol
Terphenyl-d_{14}	Phenol-d_6

5.3.1.1 Prepare a surrogate standard spiking solution in methanol that contains the base/neutral compounds at a concentration of 100 ug/mL, and the acid compounds at 200 ug/mL for water and sediment/soil samples (low- and medium-level). For waste samples, the concentration should be 500 ug/mL for base/neutrals and 1000 ug/mL for acids.

5.3.2 **Organochlorine pesticide surrogate spiking solution:** The following are recommended surrogate standards for organochlorine pesticides.

Organochlorine pesticides

Dibutylchlorendate (DBC)
2,4,5,6-Tetrachloro-meta-xylene (TCMX)

5.3.2.1 Prepare a surrogate standard spiking solution at a concentration of 1 ug/mL in acetone for water and sediment/soil samples. For waste samples, the concentration should be 5 ug/mL.

5.3.3 **Purgeable surrogate spiking solution:** The following are recommended surrogate standards for volatile organics.

Purgeable organics

p-Bromofluorobenzene
1,2-Dichloroethane-d_4
Toluene-d_8

5.3.3.1 Prepare a surrogate spiking solution (as described in Paragraph 5.2.1 or through secondary dilution of the stock standard) in methanol containing the surrogate standards at a concentration of 25 ug/mL.

5.4 Matrix spike standards: Select five or more analytes from each analyte group for use in a spiking solution. The following are recommended matrix spike standard mixtures for a few analyte groups. These compounds, or others that better correspond to the analyte group, may be used for other analyte groups as well.

5.4.1 **Base/neutral and acid matrix spiking solution:** Prepare a spiking solution in methanol that contains each of the following base/neutral compounds at 100 ug/mL and the acid compounds at 200 ug/mL for water and sediment/soil samples. The concentration of these compounds should be five times higher for waste samples.

Base/neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

5.4.2 **Organochlorine pesticide matrix spiking solution:** Prepare a spiking solution in acetone or methanol that contains the following pesticides in the concentrations specified for water and sediment/soil. The concentration should be five times higher for waste samples.

Pesticide	Concentration (ug/mL)
Lindane	0.2
Heptachlor	0.2
Aldrin	0.2
Dieldrin	0.5
Endrin	0.5
4,4'-DDT	0.5

5.4.3 **Purgeable matrix spiking solution:** Prepare a spiking solution in methanol that contains the following compounds at a concentration of 25 ug/mL.

Purgeable organics

1,1-Dichloroethene
Trichloroethene
Chlorobenzene
Toluene
Benzene

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to the Organic Analyte Chapter, Section 4.1.

7.0 PROCEDURE

7.1 Semivolatile organic sample extraction: Water, soil/sediment, sludge, and waste samples requiring analysis for base/neutral and acid extractables and/or organochlorine pesticides must undergo solvent extraction prior to analysis. This manual contains four methods that may be used for this purpose: Method 3510; Method 3520; Method 3540; and Method 3550. The method that should be used on a particular sample, is highly dependent upon the physical characteristics of that sample. Therefore, review these four methods prior to choosing one in particular. Appropriate surrogate standards and, if necessary, matrix spiking solutions are added to the sample prior to extraction for all four methods.

7.1.1 **Method 3510:** Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is solvent extracted using a separatory funnel. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Method 3520 should be used if an emulsion forms between the solvent-sample phases, which can not be broken up by mechanical techniques.

7.1.2 **Method 3520:** Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is extracted with an organic solvent in a continuous liquid-liquid extractor. The solvent must have a density greater than that of the sample. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. The limitations of Method 3510 concerning solvent-sample phase separation do not interfere with this procedure.

7.1.3 **Method 3540:** This is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis.

7.1.4 **Method 3550:** This method is applicable to the extraction of nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes using the technique of sonication. Two procedures are detailed depending upon the expected concentration of organics in the sample; a low concentration and a high concentration method. In both, a known weight of sample is mixed with anhydrous sodium sulfate and solvent extracted using sonication. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis.

7.1.5 **Method 3580:** This method describes the technique of solvent dilution of non-aqueous waste samples. It is designed for wastes that may contain organic chemicals at a level greater than 20,000 mg/kg and that are soluble in the dilution solvent.

7.2 Volatile organic sample preparation: There are three methods for volatile sample preparation: Method 5030; Method 5040; and direct injection. Method 5030 is the most widely applicable procedure for analysis of volatile organics, while the direct injection technique may have limited applicability to aqueous matrices.

7.2.1 **Method 5030:** This method describes the technique of purge-and-trap for the introduction of purgeable organics into a gas chromatograph. This procedure is applicable for use with aqueous samples directly and to solids, wastes, soils/sediments, and water-miscible liquids following appropriate preparation. An inert gas is bubbled through the sample, which will efficiently transfer the purgeable organics from the aqueous phase to the vapor phase. The vapor phase is swept through a sorbent trap where the purgeables are trapped. After purging is completed, the trap is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. Prior to application of the purge-and-trap procedure, all samples (including blanks, spikes, and duplicates) should be spiked with surrogate standards and, if required, with matrix spiking compounds.

7.2.2 **Method 5040:** This method is applicable to the investigation of sorbent cartridges from volatile organic sampling train (VOST).

7.3 Sample analysis: Following preparation of a sample by one of the methods described above, the sample is ready for further analysis. For samples requiring volatile organic analysis, application of one of the three methods described above is followed directly by gas chromatographic analysis (Methods 8010, 8015, 8020, or 8030). Samples prepared for semivolatile analysis may, if necessary, undergo cleanup (See Method 3600) prior to application of a specific determinative method.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific guidance on quality control procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of a reagent water blank that all glassware and reagents are interference free. Each time a set of samples are processed, a method blank(s) should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.3 Surrogate standards should be added to all samples when specified in the appropriate determinative method in Chapter Four, Section 4.3.

8.4 A reagent blank, a matrix spike, and a duplicate or matrix spike duplicate must be performed for each analytical batch (up to a maximum of 20 samples) analyzed.

8.5 For GC or GC/MS analysis, the analytical system performance must be verified by analyzing quality control (QC) check samples. Method 8000, Section 8.0 discusses in detail the process of verification; however, preparation of the QC check sample concentrate is dependent upon the method being evaluated.

8.5.1 **Volatile organic QC check samples:** QC check sample concentrates containing each analyte of interest are spiked into reagent water (defined as the QC check sample) and analyzed by purge-and-trap (Method 5030). The concentration of each analyte in the QC check sample is 20 ug/L. The evaluation of system performance is discussed in detail in Method 8000, beginning with Paragraph 8.6.

8.5.2 **Semivolatile organic QC check samples:** To evaluate the performance of the analytical method, the QC check samples must be handled in exactly the same manner as actual samples. Therefore, 1.0 mL of the QC check sample concentrate is spiked into each of four 1-L aliquots of reagent water (now called the QC check sample), extracted, and then analyzed by GC. The variety of semivolatile analytes which may be analyzed by GC is such that the concentration of the QC check sample concentrate is different for the different analytical techniques presented in the manual. Method 8000 discusses in detail the procedure of verifying the detection system once the QC check sample has been prepared. The concentrations of the QC check sample concentrate for the various methods are as follows:

8.5.2.1 Method 8040 - Phenols: The QC check sample concentrate should contain each analyte at a concentration of 100 ug/mL in 2-propanol.

8.5.2.2 Method 8060 - Phthalate esters: The QC check sample concentrate should contain the following analytes at the following concentrations in acetone: butyl benzyl phthalate, 10 ug/mL; bis(2-ethylhexyl)phthalate, 50 ug/mL; di-n-octylphthalate, 50 ug/mL; and any other phthalate at 25 ug/mL.

8.5.2.3 Method 8080 - Organochlorine pesticides and PCBs: The QC check sample concentrate should contain each single-component analyte at the following concentrations in acetone: 4,4'-DDD, 10 ug/mL; 4,4'-DDT, 10 ug/mL; endosulfan II, 10 ug/mL; endosulfan sulfate, 10 ug/mL; and any other single-component pesticide at 2 ug/mL. If the method is only to be used to analyze PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 ug/mL in acetone.

8.5.2.4 Method 8090 - Nitroaromatics and Cyclic Ketones: The QC check sample concentrate should contain each analyte at the following concentrations in acetone: each dinitrotoluene at 20 ug/mL; and isophorone and nitrobenzene at 100 ug/mL.

8.5.2.5 Method 8100 - Polynuclear aromatic hydrocarbons: The QC check sample concentrate should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 ug/mL; acenaphthylene, 100 ug/mL; acenaphthene, 100 ug/mL; fluorene, 100 ug/mL; phenanthrene, 100 ug/mL; anthracene, 100 ug/mL; benzo(k)fluoranthene 5 ug/mL; and any other PAH at 10 ug/mL.

8.5.2.6 Method 8120 - Chlorinated hydrocarbons: The QC check sample concentrate should contain each analyte at the following concentrations in acetone: hexachloro-substituted hydrocarbons, 10 ug/mL; and any other chlorinated hydrocarbon, 100 ug/mL.

9.0 METHOD PERFORMANCE

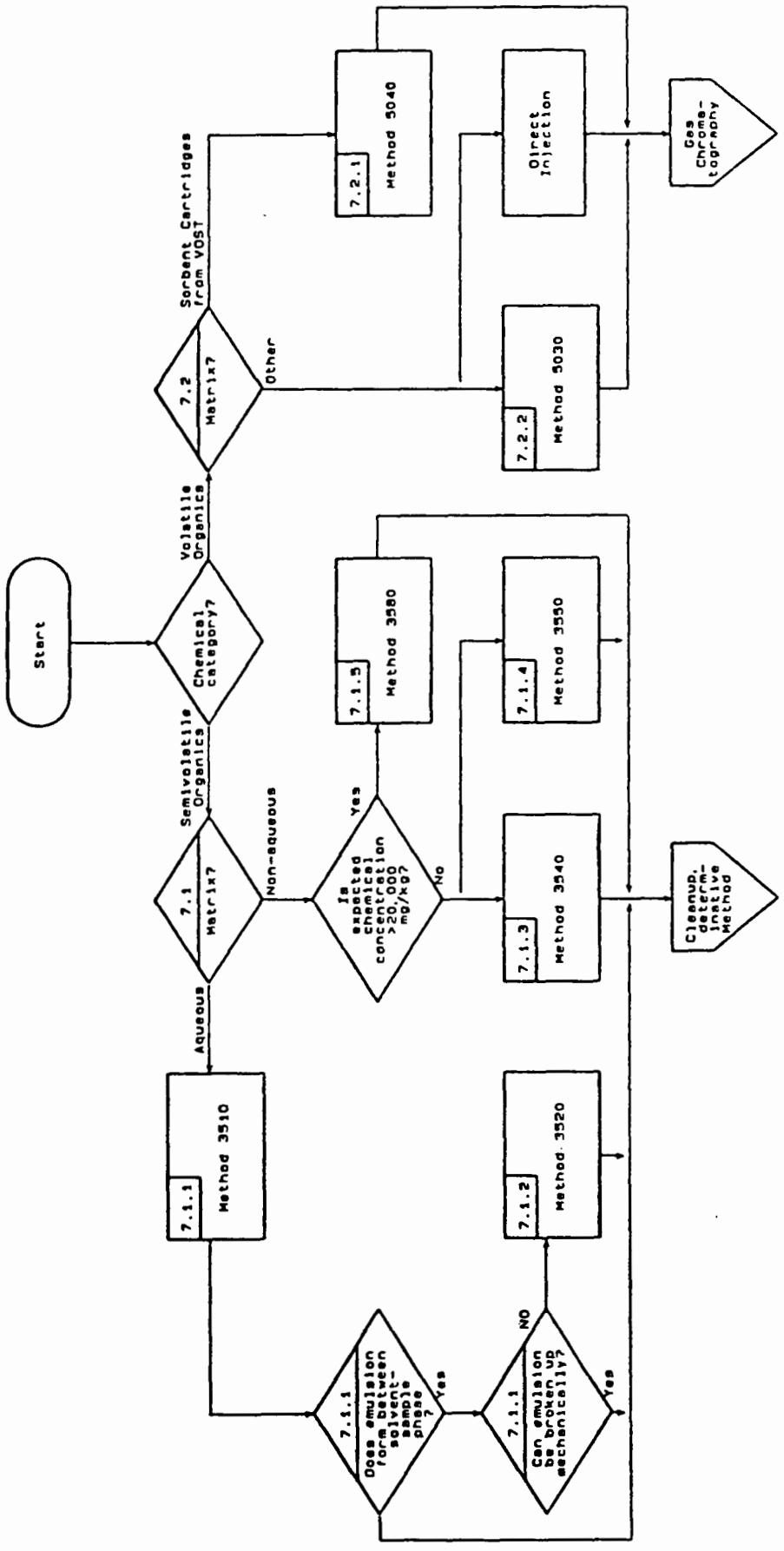
9.1 The recovery of surrogate standards is used to monitor unusual matrix effects, sample processing problems, etc. The recovery of matrix spiking compounds indicates the presence or absence of unusual matrix effects.

9.2 The performance of this method will be dictated by the overall performance of the sample preparation in combination with the analytical determinative method.

10.0 REFERENCES

10.1 None required.

METHOD 3500
ORGANIC EXTRACTION AND SAMPLE PREPARATION



METHOD 3510

SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative methods described in Section 4.3 of Chapter Four.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, at a specified pH (see Table 1), is serially extracted with methylene chloride using a separatory funnel. The extract is dried, concentrated, and, as necessary, exchanged into a solvent compatible with the cleanup or determinative step to be used.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Separatory funnel: 2-liter, with Teflon stopcock.

4.2 Drying column: 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus:

4.3.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

TABLE 1. SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040	< 2	none	2-propanol	hexane	1.0	1.0, 10.0[a]
8060	as received	none	hexane	hexane	2.0	10.0
8080	5-9	none	hexane	hexane	10.0	10.0
8090	5-9	none	hexane	hexane	2.0	1.0
8100	as received	none	none	cyclohexane	2.0	1.0
8120	as received	none	hexane	hexane	2.0	1.0
8140	6-8	none	hexane	hexane	10.0	10.0
8250[b]	>11	< 2	none	-	-	1.0
8270[b]	>11	< 2	none	-	-	1.0
8310	as received	none	acetonitrile	-	-	1.0

[a] Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

[b] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

4.3.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.6 Vials: Glass, 2-mL capacity with Teflon-lined screw cap.

4.7 pH indicator paper: pH range including the desired extraction pH.

4.8 Erlenmeyer flask: 250-mL.

4.9 Syringe: 5-mL.

4.10 Graduated cylinder: 1-liter.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2 Sodium hydroxide solution, 10 N: (ACS) Dissolve 40 g NaOH in reagent water and dilute to 100 mL.

5.3 Sodium sulfate: (ACS) Granular, anhydrous (purified by heating at 400°C for 4 hr in a shallow tray).

5.4 Sulfuric acid solution (1:1): Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

5.5 Extraction/exchange solvent: Methylene chloride, hexane, 2-propanol, cyclohexane, acetonitrile (pesticide quality or equivalent).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Using a 1-liter graduated cylinder, measure 1 liter of sample and transfer it to the separatory funnel. Add 1.0 mL of the surrogate standards to all samples, spikes, and blanks (see Method 3500 for details on the surrogate standard solution and the matrix spike solution). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/uL of each base/neutral analyte and 200 ng/uL of each acid analyte in the extract to be analyzed (assuming a 1 uL injection). If Method 3640, Gel-permeation cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.2 Check the pH of the sample with wide-range pH paper and, if necessary, adjust the pH to that indicated in Table 1 for the specific determinative method that will be used to analyze the extract.

7.3 Add 60 mL of methylene chloride to the separatory funnel.

7.4 Seal and shake the separatory funnel vigorously for 1-2 min with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once.

7.5 Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the solvent extract in an Erlenmeyer flask. If the emulsion cannot be broken (recovery of <80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Method 3520.

7.6 Repeat the extraction two more times using fresh portions of solvent (steps 7.3 through 7.5). Combine the three solvent extracts.

7.7 If further pH adjustment and extraction is required, adjust the pH of the aqueous phase to the desired pH indicated in Table 1. Serially extract three times with 60 mL of methylene chloride, as outlined in Paragraphs 7.3 through 7.5. Collect and combine the extracts and label the combined extract appropriately.

7.8 If performing GC/MS analysis (Method 8250 or 8270), the acid and base/neutral extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid and

base/neutral extracts may be preferable (e.g., if for regulatory purposes the presence or absence of specific acid or base/neutral compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.9 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.10 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20-30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

7.11 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Synder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10-20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

7.12 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent, a new boiling chip, and re-attach the Snyder column. Concentrate the extract, as described in Paragraph 7.11, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.13 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Paragraph 7.14 or adjusted to 10.0 mL with the solvent last used.

7.14 If further concentration is indicated in Table 1, add another clean boiling chip to the concentrator tube and attach a two-ball micro Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Synder column and rinse the flask and its lower joints into the concentrator tube with 0.2 mL of extraction solvent. Adjust the final volume to 1.0-2.0 mL, as indicated in Table 1, with solvent.

7.15 The extract obtained (from either Paragraph 7.13 or 7.14) may now be analyzed for analyte content using a variety of organic techniques. If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days, it should be transferred to a Teflon-sealed screw-cap vial and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

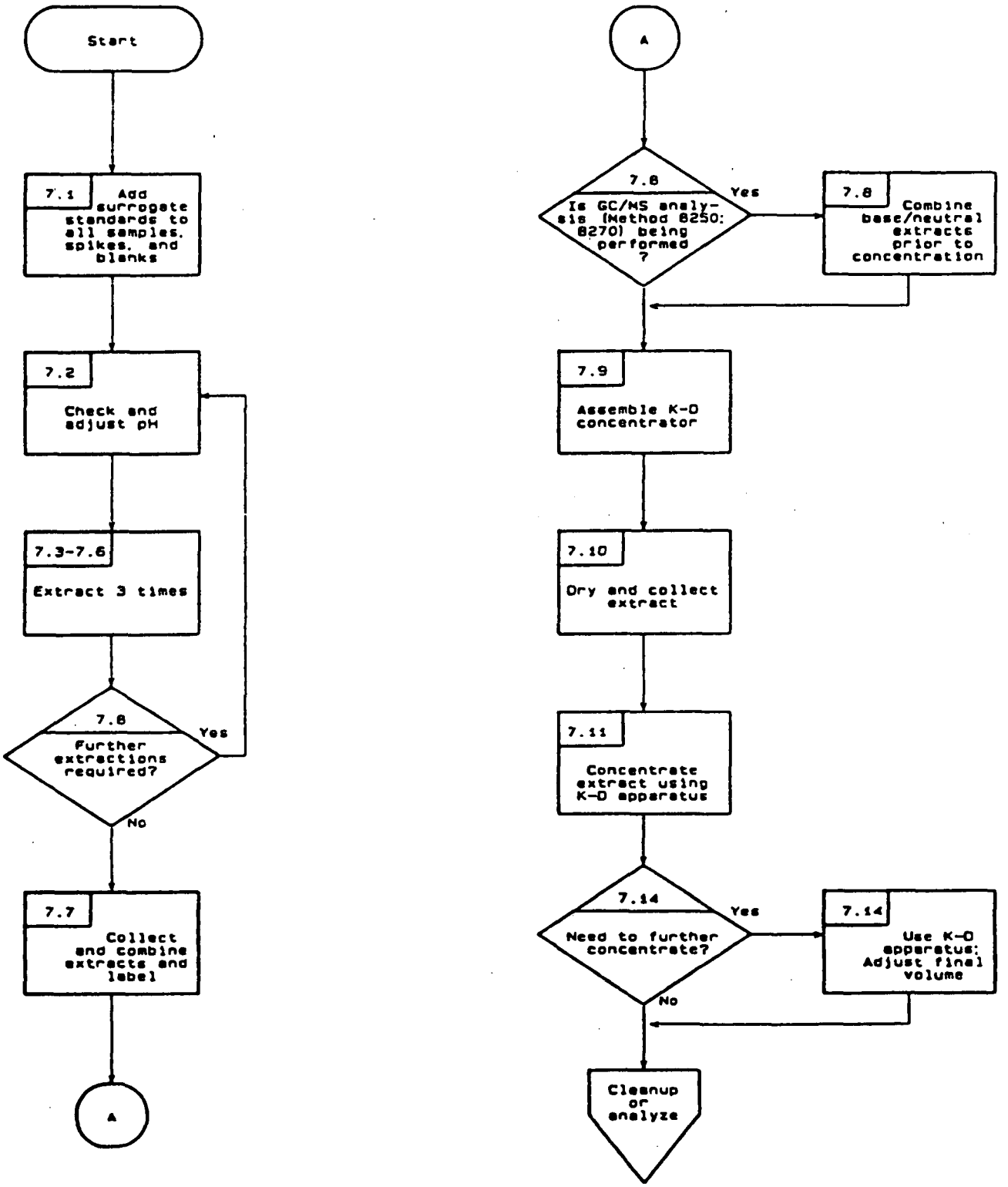
9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

METHOD 3510

SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION



METHOD 3520

CONTINUOUS LIQUID-LIQUID EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative steps described in Section 4.3 of Chapter Four.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly soluble organics in preparation for a variety of chromatographic procedures.

1.3 Method 3520 is designed for extraction solvents with greater density than the sample. Continuous extraction devices are available for extraction solvents that are less dense than the sample. The analyst must demonstrate the effectiveness of any such automatic extraction device before employing it in sample extraction.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, is placed into a continuous liquid-liquid extractor, adjusted, if necessary, to a specific pH (see Table 1), and extracted with organic solvent for 18-24 hr. The extract is dried, concentrated, and, as necessary, exchanged into a solvent compatible with the determinative step being employed.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Continuous liquid-liquid extractor: Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf Extractor -- Ace Glass Company, Vineland, New Jersey, P/N 6841-10, or equivalent).

4.2 Drying column: 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

TABLE 1. SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040	< 2	none	2-propanol	hexane	1.0	1.0, 10.0[a]
8060	as received	none	hexane	hexane	2.0	10.0
8080	5–9	none	hexane	hexane	10.0	10.0
8090	5–9	none	hexane	hexane	2.0	1.0
8100	as received	none	none	cyclohexane	2.0	1.0
8120	as received	none	hexane	hexane	2.0	1.0
8140[b]	6–8	none	hexane	hexane	10.0	10.0
8250[b]	>11	< 2	none	-	-	1.0
8270[b]	>11	< 2	none	-	-	1.0
8310	as received	none	acetonitrile	-	-	1.0

[a] Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

[b] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

4.3 Kuderna-Danish (K-D) apparatus:

4.3.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.3.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.6 Vials: Glass, 2-mL capacity, with Teflon-lined screw cap.

4.7 pH indicator paper: pH range including the desired extraction pH.

4.8 Heating mantle: Rheostat controlled.

4.9 Syringe: 5-mL.

4.10 Graduated cylinder: 1-liter.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2 Sodium hydroxide solution, 10 N: (ACS) Dissolve 40 g NaOH in reagent water and dilute to 100 mL.

5.3 Sodium sulfate: (ACS) Granular, anhydrous (purified by heating at 400°C for 4 hr in a shallow tray).

5.4 Sulfuric acid solution (1:1): Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

5.5 Extraction/exchange solvent: Methylene chloride, hexane, 2-propanol, cyclohexane, acetonitrile (pesticide quality or equivalent).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Using a graduated cylinder, measure out 1 liter (nominal) of sample and transfer it to the continuous extractor. Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to the pH indicated in Table 1. Pipet 1.0 mL of the surrogate standard spiking solution into each sample into the extractor and mix well. (See Method 3500 for details on the surrogate standard solution and the matrix spike solution.) For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount of the surrogates and matrix spiking compounds added to the sample should result in a final concentration of 100 ng/uL of each base/neutral analyte and 200 ng/uL of each acid analyte in the extract to be analyzed (assuming a 1 uL injection). If Method 3640, Gel-permeation cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.2 Add 300-500 mL of methylene chloride to the distilling flask. Add several boiling chips to the flask.

7.3 Add sufficient reagent water to the extractor to ensure proper operation and extract for 18-24 hr.

7.4 Allow to cool; then detach the boiling flask. If extraction at a secondary pH is not required (see Table 1), the extract is dried and concentrated as described in Section 7.7 through 7.11.

7.5 Carefully, while stirring, adjust the pH of the aqueous phase to <2 with sulfuric acid (1:1). Attach a clean distilling flask containing 500 mL of methylene chloride to the continuous extractor. Extract for 18-24 hr, allow to cool, and detach the distilling flask.

7.6 If performing GC/MS analysis (Method 8250 or 8270), the acid and base/neutral extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid and base/neutral extracts may be preferable (e.g., if for regulatory purposes the presence or absence of specific acid or base/neutral compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.7 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.8 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D

concentrator. Rinse the flask which contained the solvent extract with 20-30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

7.9 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of extraction solvent.

7.10 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent, a new boiling chip, and re-attach the Snyder column. Concentrate the extract, as described in Paragraph 7.9, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.11 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Paragraph 7.12 or adjusted to 10.0 mL with the solvent last used.

7.12 Add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Synder column, rinse the flask and its lower joints into the concentrator tube with 0.2 mL of methylene chloride or exchange solvent, and adjust the final volume to 1.0-2.0 mL, as indicated in Table 1, with solvent.

7.13 The extracts obtained may now be analyzed for analyte content using a variety of organic techniques (see Section 4.3 of this chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days, it should be transferred to a Teflon-sealed screw-cap vial and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample-preparation procedures.

9.0 METHOD PERFORMANCE

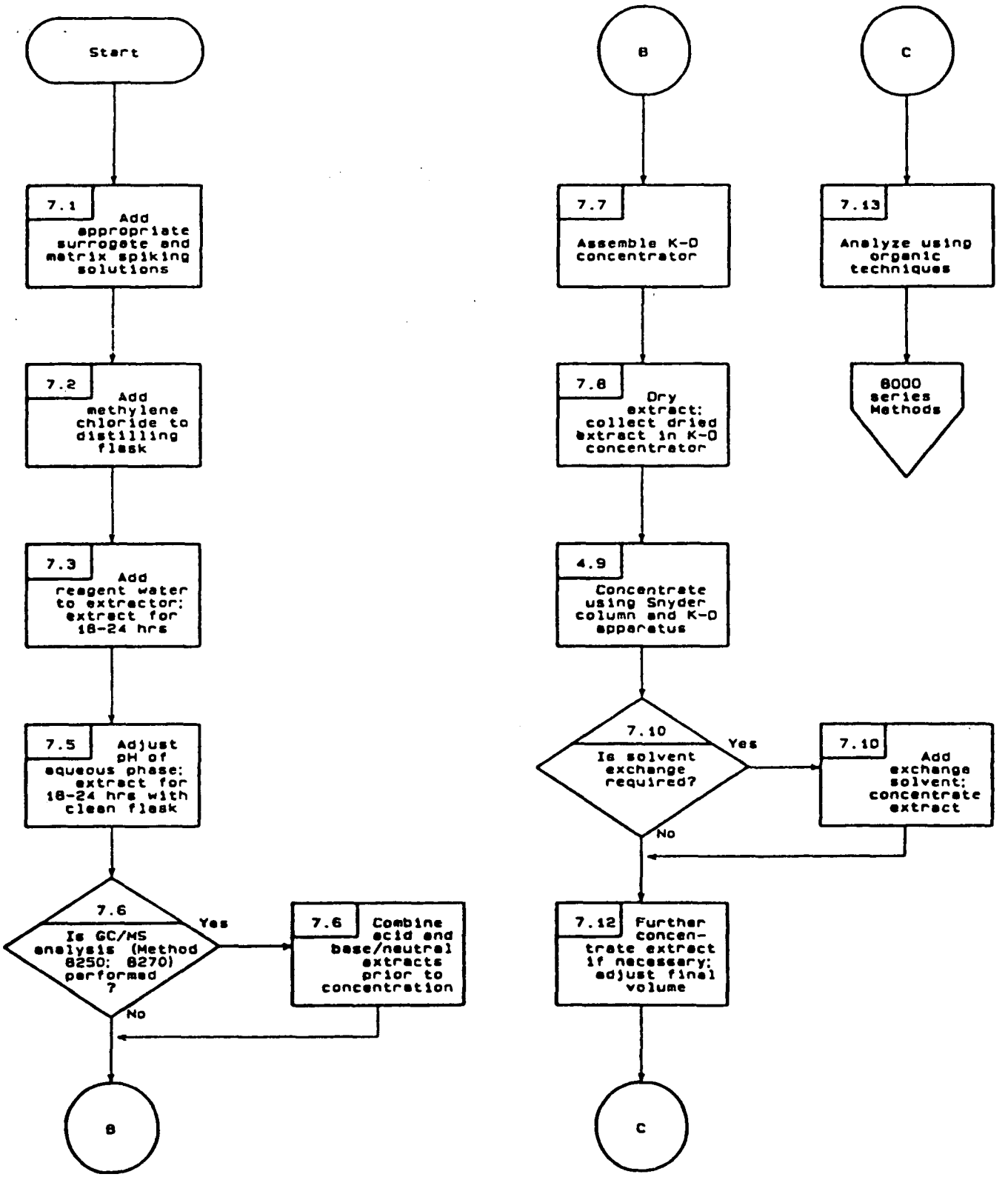
9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

METHOD 3520

CONTINUOUS LIQUID-LIQUID EXTRACTION



Revision 0
Date September 1986

METHOD 3540

SOXHLET EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3540 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

2.0 SUMMARY OF METHOD

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is then dried, concentrated, and, as necessary, exchanged into a solvent compatible with the cleanup or determinative step being employed.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extractor: 40-mm I.D., with 500-mL round-bottom flask.

4.2 Drying column: 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus:

4.3.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.3.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.6 Vials: Glass, 2-mL capacity, with Teflon-lined screw cap.

4.7 Glass or paper thimble or glass wool: Contaminant free.

4.8 Heating mantle: Rheostat controlled.

4.9 Syringe: 5-mL.

4.10 Apparatus for determining percent moisture:

4.10.1 **Oven:** Drying.

4.10.2 **Desiccator.**

4.10.3 **Crucibles:** Porcelain.

4.11 Apparatus for grinding: If the sample will not pass through a 1-mm standard sieve or cannot be extruded through a 1-mm opening, it should be processed into a homogeneous sample that meets these requirements. Fisher Mortar Model 155 Grinder, Fisher Scientific Co., Catalogue Number 8-323, or an equivalent brand and model, is recommended for sample processing. This grinder should handle most solid samples, except gummy, fibrous, or oily materials.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2 Sodium sulfate: (ACS) Granular anhydrous (purified by washing with methylene chloride followed by heating at 400°C for 4 hr in a shallow tray).

5.3 Extraction solvents:

5.3.1 Soil/sediment and aqueous sludge samples shall be extracted using either of the following solvent systems.

5.3.1.1 Toluene/Methanol: 10:1 (v/v), pesticide quality or equivalent.

5.3.1.2 Acetone/Hexane: 1:1 (v/v), pesticide quality or equivalent.

5.3.2 Other samples shall be extracted using the following:

5.3.2.1 Methylene chloride: pesticide quality or equivalent.

5.4 Exchange solvents: Hexane, 2-propanol, cyclohexane, acetonitrile (pesticide quality or equivalent).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sample handling:

7.1.1 **Sediment/soil samples:** Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 **Waste samples:** Samples consisting of multiphases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.1.3 **Dry waste samples amenable to grinding:** Grind or otherwise subdivide the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.2 Determination of percent moisture: In certain cases, sample results are desired based on a dry-weight basis. When such data is desired, a portion of sample for moisture determination should be weighed out at the same time as the portion used for analytical determination.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\frac{\text{g of sample - g of dry sample}}{\text{g of sample}} \times 100 = \% \text{ moisture}$$

7.3 Blend 10 g of the solid sample with 10 g of anhydrous sodium sulfate and place in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble. Add 1.0 mL of the surrogate standard spiking solution onto the sample (See Method 3500 for details on the surrogate standard and matrix spiking solutions.) For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/uL of each base/neutral analyte and 200 ng/uL of each acid analyte in the extract to be analyzed (assuming a 1 uL injection). If Method 3640, Gel-permeation cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.4 Place 300 mL of the extraction solvent (Section 5.3) into a 500-mL round-bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hr.

7.5 Allow the extract to cool after the extraction is complete.

7.6 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.7 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Wash the extractor flask and sodium sulfate column with 100-125 mL of extraction solvent to complete the quantitative transfer.

7.8 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

7.9 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip, and re-attach the Snyder column. Concentrate the extract as described in Paragraph 7.6, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.10 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Paragraph 7.9 or adjusted to 10.0 mL with the solvent last used.

TABLE 1. SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040[a]	as received	2-propanol	hexane	1.0	1.0, 10.0[b]
8060	as received	hexane	hexane	2.0	10.0
8080	as received	hexane	hexane	10.0	10.0
8090	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8120	as received	hexane	hexane	2.0	1.0
8140	as received	hexane	hexane	10.0	10.0
8250[a,c]	as received	none	-	-	1.0
8270[a,c]	as received	none	-	-	1.0
8310	as received	acetonitrile	-	-	1.0

[a]To obtain separate acid and base/neutral extracts, Method 3650 should be performed following concentration of the extract to 10.0 mL.

[b]Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

[c]The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

7.11 If further concentration is indicated in Table 1, add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 0.2 mL of solvent. Adjust the final volume to 1.0-2.0 mL, as indicated in Table 1, with solvent.

7.12 The extracts obtained may now be analyzed for analyte content using a variety of organic techniques (see Section 4.3 of this chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days, it should be transferred to a Teflon-sealed screw-cap vial and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

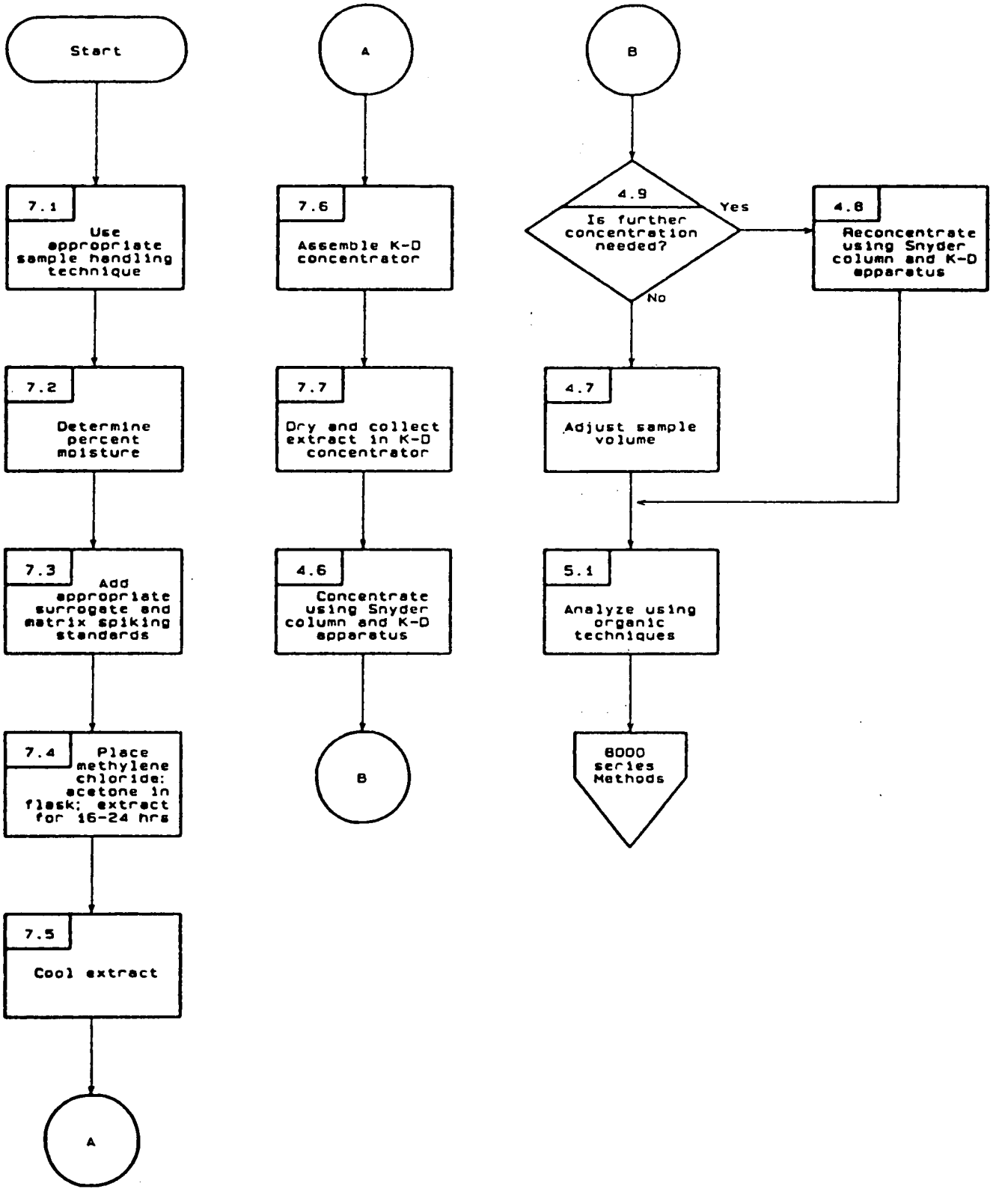
9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

METHOD 3540

SOXHLET EXTRACTION



Revision 0
Date September 1986

METHOD 3550

SONICATION EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3550 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. The sonication process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 The method is divided into two sections, based on the expected concentration of organics in the sample. The low concentration method (individual organic components of $\leq$20 mg/kg) uses a larger sample size and a more rigorous extraction procedure (lower concentrations are more difficult to extract). The high concentration method (individual organic components of $>$20 mg/kg) is much simpler and therefore faster.

1.3 It is highly recommended that the extracts be cleaned up prior to analysis. See Cleanup, Section 4.2.2 of Chapter Four, for applicable methods.

2.0 SUMMARY OF METHOD

2.1 Low concentration method: A 30-g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted three times using sonication. The extract is separated from the sample by vacuum filtration or centrifugation. The extract is ready for cleanup and/or analysis following concentration.

2.2 High concentration method: A 2-g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted once using sonication. A portion of the extract is removed for cleanup and/or analysis.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Apparatus for grinding: If the sample will not pass through a 1-mm standard sieve or cannot be extruded through a 1-mm opening, it should be processed into a homogeneous sample that meets these requirements. Fisher Mortar Model 155 Grinder, Fisher Scientific Co., Catalogue Number 8-323, or an equivalent brand and model, is recommended for sample processing. This grinder should handle most solid samples, except gummy, fibrous, or oily materials.

4.2 Sonication: A horn-type sonicator equipped with a titanium tip should be used. The following sonicator, or an equivalent brand and model, is recommended:

Ultrasonic cell disrupter: Heat Systems - Ultrasonics, Inc., Model W-385 (475 watt) sonicator or equivalent (Power wattage must be a minimum of 375 with pulsing capability and No. 200 1/2" Tapped Disrupter Horn) plus No. 207 3/4" Tapped Disrupter Horn, and No. 419 1/8" Standard Tapered microtip probe.

4.3 Sonabox: Recommended with above disrupters for decreasing cavitation sound (Heat Systems - Ultrasonics, Inc., Model 432B or equivalent).

4.4 Apparatus for determining percent moisture:

4.4.1 **Oven:** Drying.

4.4.2 **Desiccator.**

4.4.3 **Crucibles:** Porcelain.

4.5 Pasteur glass pipets: Disposable, 1-mL.

4.6 Beakers: 400-mL.

4.7 Vacuum filtration apparatus:

4.7.1 **Buchner funnel.**

4.7.2 **Filter paper:** Whatman No. 41 or equivalent.

4.8 Kuderna-Danish (K-D) apparatus:

4.8.1 **Concentrator tube:** 10-mL graduated (Kontes K-570050-1025 or equivalent).

4.8.2 **Evaporator flask:** 500-mL (Kontes K-570001-0500 or equivalent).

4.8.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.8.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.9 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.10 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.11 Balance: Top-loading, capable of accurately weighing 0.01 g.

4.12 Vials and caps: 2-mL for GC auto-sampler.

4.13 Glass scintillation vials: At least 20-mL, with screw-cap and Teflon or aluminum foil liner.

4.14 Spatula: Stainless steel or Teflon.

4.15 Drying column: 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.16 Syringe: 5-mL.

5.0 REAGENTS

5.1 Sodium sulfate: Anhydrous and reagent grade, heated at 400°C for 4 hr, cooled in a desiccator, and stored in a glass bottle. Baker anhydrous powder, catalog #73898, or equivalent.

5.2 Extraction solvents: Methylene chloride:acetone (1:1, v:v), methylene chloride, hexane (pesticide quality or equivalent).

5.3 Exchange solvents: Hexane, 2-propanol, cyclohexane, acetonitrile (pesticide quality or equivalent).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sample handling:

7.1.1 Sediment/soil samples: Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 Waste samples: Samples consisting of multiphases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.1.3 **Dry waste samples amenable to grinding:** Grind or otherwise subdivide the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.2 Determination of percent moisture: In certain cases, sample results are desired based on a dry-weight basis. When such data is desired, a portion of sample for moisture determination should be weighed out at the same time as the portion used for analytical determination.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\frac{\text{g of sample - g of dry sample}}{\text{g of sample}} \times 100 = \% \text{ moisture}$$

7.3 Determination of pH (if required): Transfer 50 g of sample to a 100-mL beaker. Add 50 mL of water and stir for 1 hr. Determine the pH of sample with glass electrode and pH meter while stirring. Discard this portion of sample.

7.4 Extraction method for samples expected to contain low concentrations of organics and pesticides ($\lesssim$20 mg/kg):

7.4.1 The following step should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample into a 400-mL beaker. Record the weight to the nearest 0.1 g. Non-porous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate using a spatula. The sample should be free-flowing at this point. Add 1 mL of surrogate standards to all samples, spikes, and blanks (see Method 3500 for details on the surrogate standard solution and the matrix spike solution). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/uL of each base/neutral analyte and 200 ng/uL of each acid analyte in the extract to be analyzed (assuming a 1 uL injection). If Method 3640, Gel-permeation cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half of the extract is lost due to loading of the GPC column. Immediately add 100 mL of 1:1 methylene chloride:acetone.

7.4.2 Place the bottom surface of the tip of the #207 3/4 in. disruptor horn about 1/2 in. below the surface of the solvent, but above the sediment layer.

7.4.3 Sonicate for 3 min, with output control knob set at 10 and with mode switch on Pulse and percent-duty cycle knob set at 50%. Do NOT use microtip probe.

7.4.4 Decant and filter extracts through Whatman No. 41 filter paper using vacuum filtration or centrifuge and decant extraction solvent.

7.4.5 Repeat the extraction two or more times with two additional 100-mL portions of solvent. Decant off the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with extraction solvent.

7.4.6 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask.

7.4.7 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Wash the extractor flask and sodium sulfate column with 100-125 mL of extraction solvent to complete the quantitative transfer.

7.4.8 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-15 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.4.9 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip, and re-attach the Snyder column. Concentrate the extract as described in Paragraph 7.4.8, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.4.10 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Paragraph 7.4.11 or adjusted to 10.0 mL with the solvent last used.

7.4.11 Add a clean boiling chip and attach a two-ball micro-Snyder column to the concentrator tube. Prewet the column by adding approximately 0.5 mL of methylene chloride or exchange solvent through the top. Place the apparatus in the hot water bath. Adjust the vertical position and the water temperature, as required, to complete the concentration in 5-10 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the liquid

TABLE 1. SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040[a]	as received	2-propanol	hexane	1.0	1.0, 10.0[b]
8060	as received	hexane	hexane	2.0	10.0
8080	as received	hexane	hexane	10.0	10.0
8090	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8120	as received	hexane	hexane	2.0	1.0
8140	as received	hexane	hexane	10.0	10.0
8250[a,c]	as received	none	-	-	1.0
8270[a,c]	as received	none	-	-	1.0
8310	as received	acetonitrile	-	-	1.0

[a] To obtain separate acid and base/neutral extracts, Method 3650 should be performed following concentration of the extract to 10.0 mL.

[b] Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

[c] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

reaches an apparent volume of approximately 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 min. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with approximately 0.2 mL of appropriate solvent. Adjust the final volume to the volume required for cleanup or for the determinative method (see Table 1).

7.4.12 Transfer the concentrated extract to a clean screw-cap vial. Seal the vial with a Teflon-lined lid and mark the level on the vial. Label with the sample number and fraction and store in the dark at 4°C until ready for analysis or cleanup.

7.5 Extraction method for samples expected to contain high concentrations of organics (>20 mg/kg):

7.5.1 Transfer approximately 2 g (record weight to the nearest 0.1 g) of sample to a 20-mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken. Cap the vial before proceeding with the next sample to avoid any cross contamination.

7.5.2 Add 2 g of anhydrous sodium sulfate to sample in the 20-mL vial and mix well.

7.5.3 Surrogate standards are added to all samples, spikes, and blanks (see Method 3500 for details on the surrogate standard solution and on the matrix spike solution). Add 2.0 mL of surrogate spiking solution to sample mixture. For the sample in each analytical batch selected for spiking, add 2.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 200 ng/uL of each base/neutral analyte and 400 ng/uL of each acid analyte in the extract to be analyzed (assuming a 1 uL injection). If Method 3640, Gel-permeation cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.5.4 Immediately add whatever volume of solvent is necessary to bring the final volume to 10.0 mL considering the added volume of surrogates and matrix spikes. Disrupt the sample with the 1/8-in. tapered microtip ultrasonic probe for 2 min at output control setting 5 and with mode switch on pulse and percent duty cycle of 50%. Extraction solvents are:

1. Nonpolar compounds, i.e., organochlorine pesticides and PCBs: hexane.

2. Extractable priority pollutants: methylene chloride.

7.5.5 Loosely pack disposable Pasteur pipets with 2- to 3-cm Pyrex glass-wool plugs. Filter the extract through the glass wool and collect

5.0 mL in a concentrator tube if further concentration is required. Follow Paragraphs 7.4.6 through 7.4.12 for details on concentration. Normally, the 5.0 mL extract is concentrated to 1.0 mL.

7.5.6 The extract is ready for cleanup or analysis, depending on the extent of interfering co-extractives.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subject to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

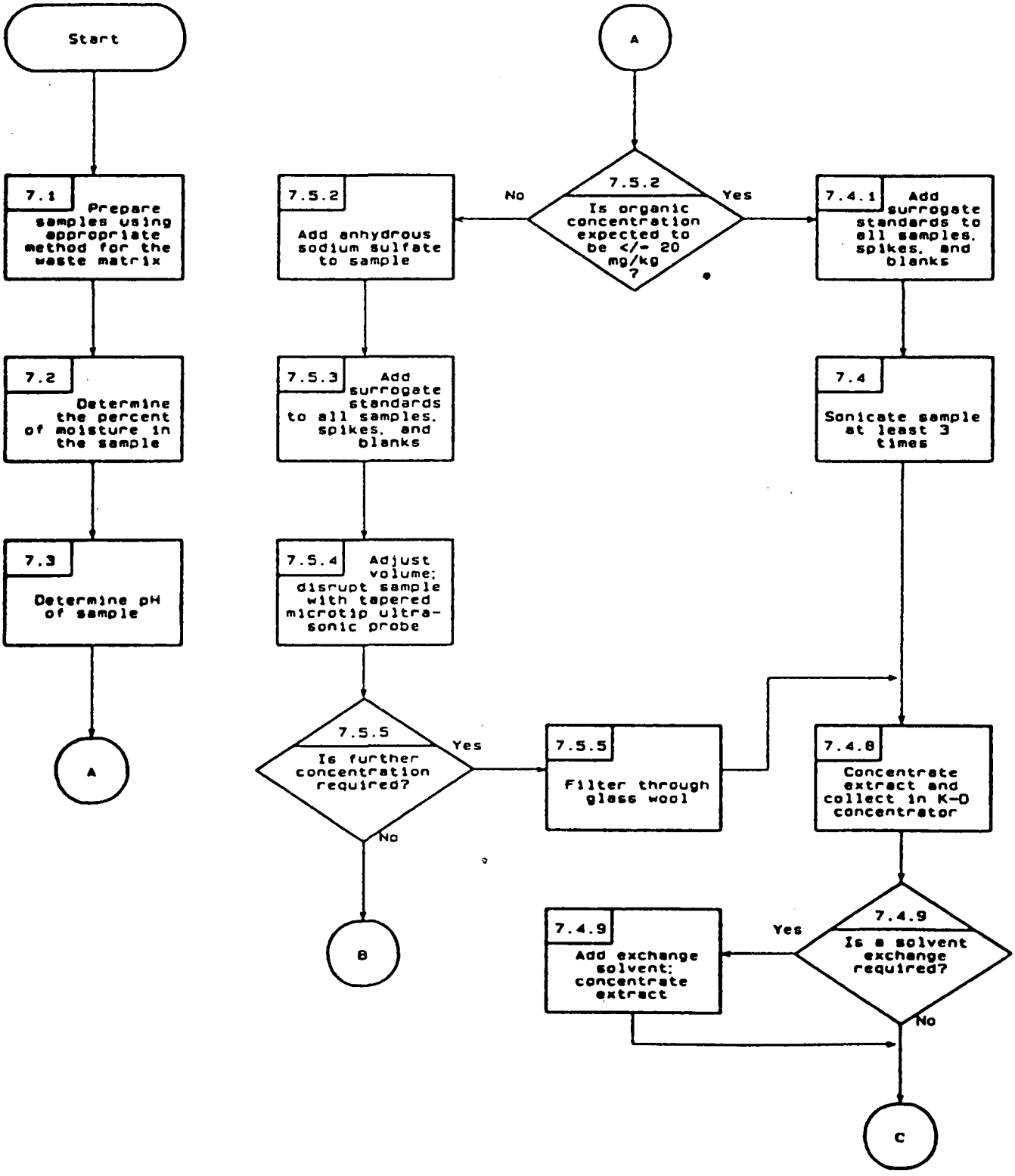
9.0 METHOD PERFORMANCE

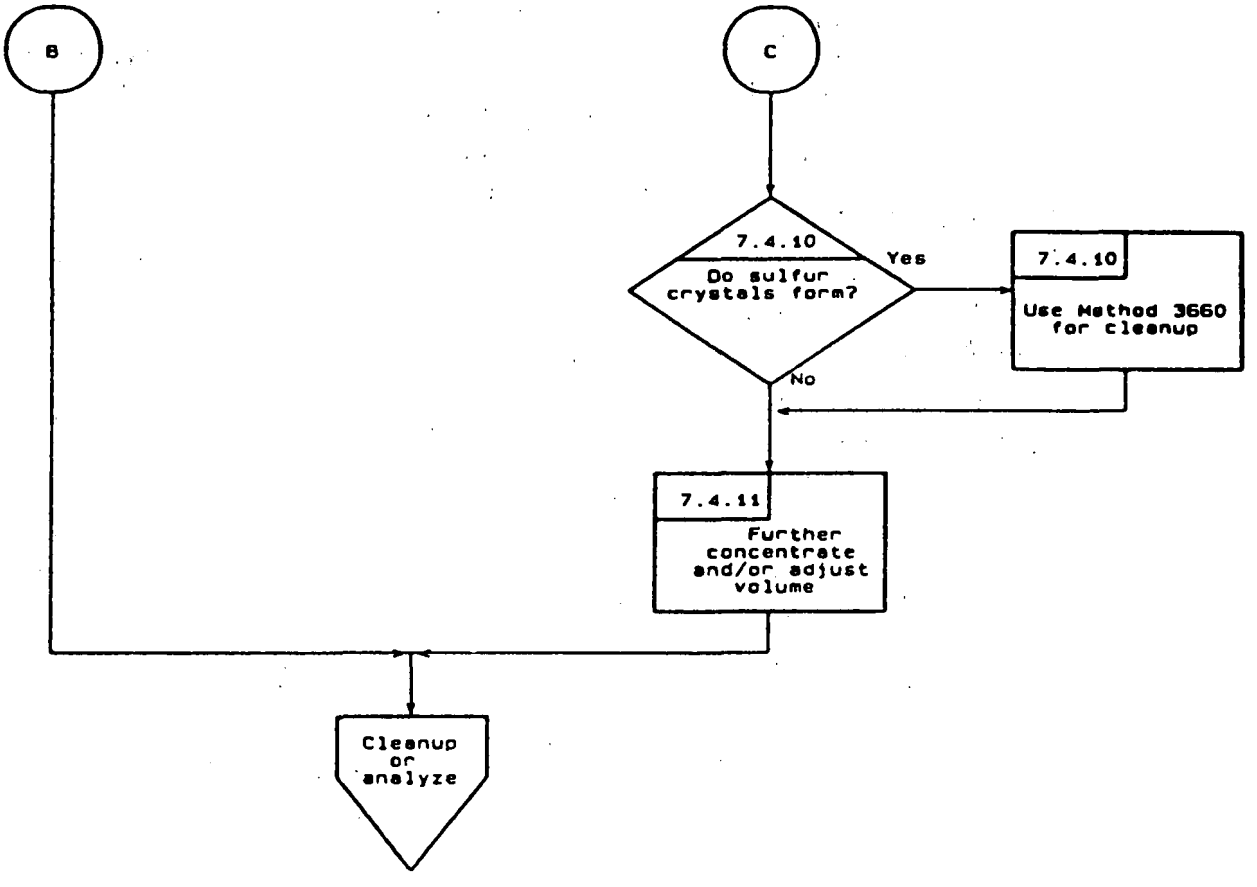
9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

2. U.S. EPA, Interlaboratory Comparison Study: Methods for Volatile and Semi-Volatile Compounds, Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, NV, EPA 600/4-84-027, 1984.


Start
7.1 Prepare samples using appropriate method for the waste matrix
7.2 Determine the percent of moisture in the sample
7.3 Determine pH of sample
A
A
7.5.2 Is organic concentration expected to be </- 20 mg/kg ?
No
Yes
7.5.2 Add anhydrous sodium sulfate to sample
7.5.3 Add surrogate standards to all samples, spikes, and blanks
7.5.4 Adjust volume; disrupt sample with tapered microtip ultra-sonic probe
7.5.5 Is further concentration required?
Yes
No
B
7.5.5 Filter through glass wool
7.4.1 Add surrogate standards to all samples, spikes, and blanks
7.4 Sonicate sample at least 3 times
7.4.8 Concentrate extract and collect in K-D concentrator
7.4.9 Is a solvent exchange required?
Yes
No
7.4.9 Add exchange solvent; concentrate extract
C


B
C
7.4.10
Do sulfur crystals form?
Yes
No
7.4.10
Use Method 3660 for cleanup
7.4.11
Further concentrate and/or adjust volume
Cleanup or analyze

METHOD 3580

WASTE DILUTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a solvent dilution of a non-aqueous waste sample prior to cleanup and/or analysis. It is designed for wastes that may contain organic chemicals at a level greater than 20,000 mg/kg and that are soluble in the dilution solvent.

1.2 It is recommended that an aliquot of the diluted sample be cleaned up. See the Cleanup section of this chapter for methods (Section 4.2.2).

2.0 SUMMARY OF METHOD

2.1 One gram of sample is weighed into a capped tube, and the sample is diluted to 10.0 mL with an appropriate solvent.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Glass scintillation vials: At least 20-mL, with Teflon or aluminum-foil-lined screw-cap.

4.2 Spatula: Stainless steel or Teflon.

4.3 Balance: Capable of weighing 100 g to the nearest 0.01 g.

4.4 Vials and caps: 2-mL for GC autosampler.

4.5 Disposable pipets: Pasteur.

4.6 Test tube rack.

4.7 Pyrex glass wool.

4.8 Volumetric flasks: 10-mL (optional).

5.0 REAGENTS

5.1 Sodium sulfate: (ACS) Granular, anhydrous (purified by heating at 400°C for 4 hr in a shallow tray).

5.2 Solvents: Methylene chloride and hexane (pesticide quality or equivalent).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Samples consisting of multiphases must be prepared by the phase separation method (Chapter Two) before extraction.

7.2 The sample dilution may be performed in a 10-mL volumetric flask. If disposable glassware is preferred, the 20-mL scintillation vial may be calibrated for use. Simply pipet 10.0 mL of extraction solvent into the scintillation vial and mark the bottom of the meniscus. Discard this solvent.

7.3 Transfer approximately 1 g of each phase (record weight to the nearest 0.1 g) of the sample to separate 20-mL vials or 10-mL volumetric flasks. Wipe the mouth of the vial with a tissue to remove any sample material. Cap the vial before proceeding with the next sample to avoid any cross-contamination.

7.4 Add 2.0 mL surrogate spiking solution to all samples and blanks. For the sample in each analytical batch selected for spiking, add 2.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 200 ng/uL of each base/neutral analyte and 400 ng/uL of each acid analyte in the extract to be analyzed (assuming a 1 uL injection). If Method 3640, Gel-permeation cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column. See Method 3500 for details on the surrogate standard and matrix spiking solutions.

7.5 Immediately dilute to 10 mL with the appropriate solvent. For compounds to be analyzed by GC/ECD, e.g., organochlorine pesticides and PCBs, the dilution solvent should be hexane. For base/neutral and acid semivolatile priority pollutants, use methylene chloride. If dilution is to be cleaned up by gel permeation chromatography (Method 3640), use methylene chloride as the dilution solvent for all compounds.

7.6 Add 2.0 g of anhydrous sodium sulfate to the sample.

7.7 Cap and shake the sample for 2 min.

7.8 Loosely pack disposable Pasteur pipets with 2-3 cm glass wool plugs. Filter the extract through the glass wool and collect 5 mL of the extract in a tube or vial.

7.9 The extract is ready for cleanup or analysis, depending on the extent of interfering co-extractives.

8.0 QUALITY CONTROL

8.1 Any reagent blanks and matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

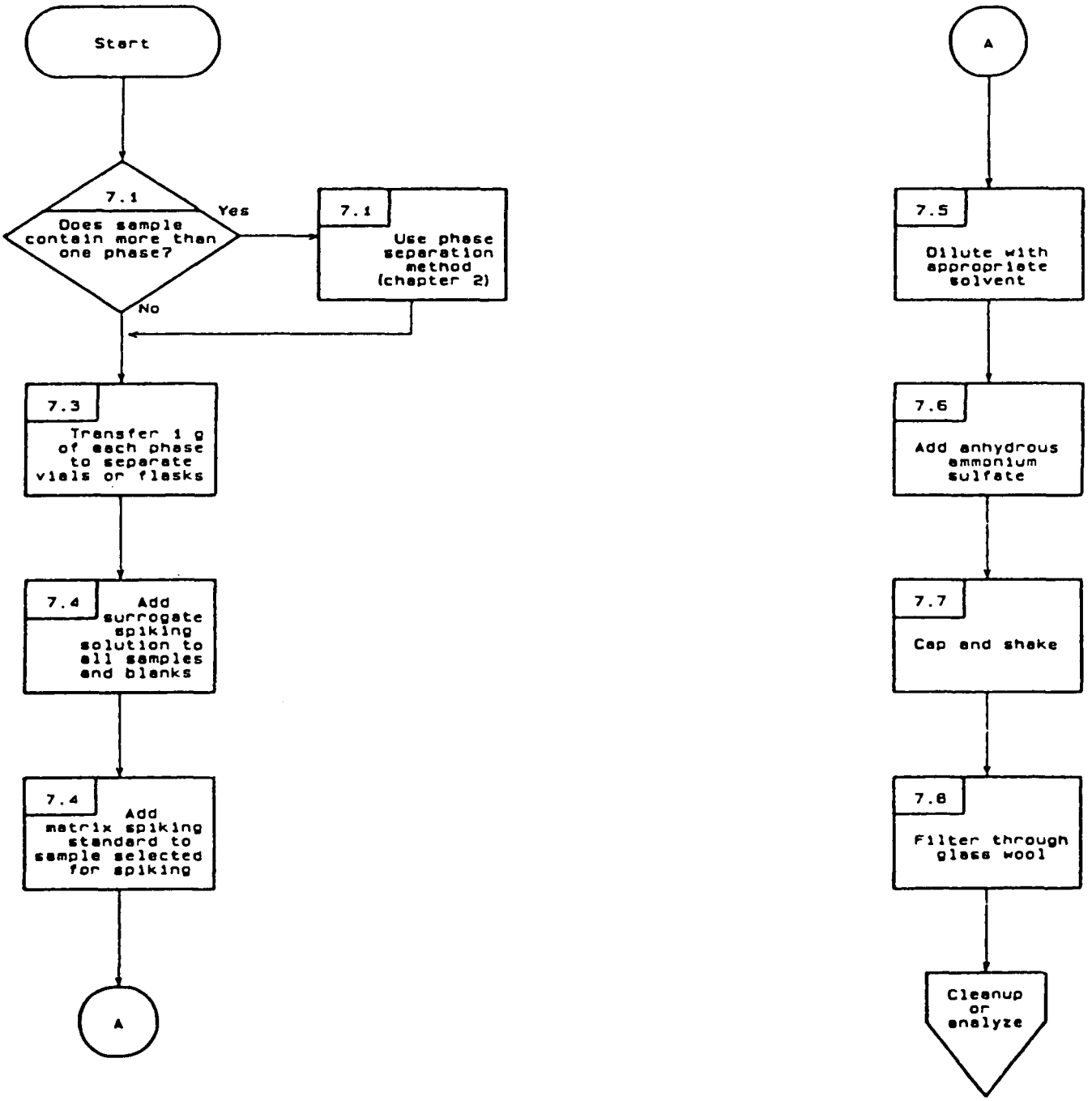
8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

10.1 None applicable.


Start
7.1
Does sample contain more than one phase?
Yes
No
7.1
Use phase separation method (chapter 2)
7.3
Transfer 1 g of each phase to separate vials or flasks
7.4
Add surrogate spiking solution to all samples and blanks
7.4
Add matrix spiking standard to sample selected for spiking
A
A
7.5
Dilute with appropriate solvent
7.6
Add anhydrous ammonium sulfate
7.7
Cap and shake
7.8
Filter through glass wool
Cleanup or analyze

METHOD 5030

PURGE-AND-TRAP

1.0 SCOPE AND APPLICATION

1.1 This method describes sample preparation and extraction for the analysis of volatile organics by a purge-and-trap procedure. The gas chromatographic determinative steps are found in Methods 8010, 8015, 8020, and 8030. Although applicable to Method 8240, the purge-and-trap procedure is already incorporated into Method 8240.

1.2 Method 5030 can be used for most volatile organic compounds that have boiling points below 200°C (vapor pressure is approximately equal to mm Hg @ 25°C) and are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax. Such compounds include low-molecular-weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

1.3 Water samples can be analyzed directly for volatile organic compounds by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in water can be determined by direct injection of the sample into the chromatographic system.

1.4 This method also describes the preparation of water-miscible liquids, solids, wastes, and soil/sediments for analysis by the purge-and-trap procedure.

2.0 SUMMARY OF METHOD

2.1 The purge-and-trap process: An inert gas is bubbled through the solution at ambient temperature, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column.

2.2 If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is combined with water in a specially designed purging chamber. It is then analyzed by purge-and-trap GC following the normal water method.

3.0 INTERFERENCES

3.1 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE plastic coating, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A field reagent blank prepared from reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by an analysis of reagent water to check for cross-contamination. The trap and other parts of the system are subject to contamination; therefore, frequent bake-out and purging of the entire system may be required.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringes: 10-uL, 25-uL, 100-uL, 250-uL, 500-uL, and 1,000 uL: These syringes should be equipped with a 20-gauge (0.006-in I.D.) needle having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device. The needle length will depend upon the dimensions of the purging device employed.

4.2 Syringe valve: Two-way, with Luer ends (three each), if applicable to the purging device.

4.3 Syringe: 5-mL, gas-tight with shutoff valve.

4.4 Balance: Analytical, capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.1 g.

4.5 Glass scintillation vials: 20-mL, with screw-caps and Teflon liners or glass culture tubes with a screw-cap and Teflon liner.

4.6 Volumetric flasks: 10-mL and 100-mL, class A with ground-glass stoppers.

4.7 Vials: 2-mL, for GC autosampler.

4.8 Spatula: Stainless steel.

4.9 Disposable pipets: Pasteur.

4.10 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.10.1 The recommended purging chamber is designed to accept 5-mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3-mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria. Alternate sample purge devices may be used, provided equivalent performance is demonstrated.

4.10.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap must contain the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap (see Figures 2 and 3). If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

4.10.3 The desorber should be capable of rapidly heating the trap to 180°C for desorption. The polymer section of the trap should not be heated higher than 180°C, and the remaining sections should not exceed 220°C during bake-out mode. The desorber design illustrated in Figures 2 and 3 meet these criteria.

4.10.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 4 and 5.

4.10.5 **Trap Packing Materials**

4.10.5.1 2,6-Diphenylene oxide polymer: 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.10.5.2 Methyl silicone packing: OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

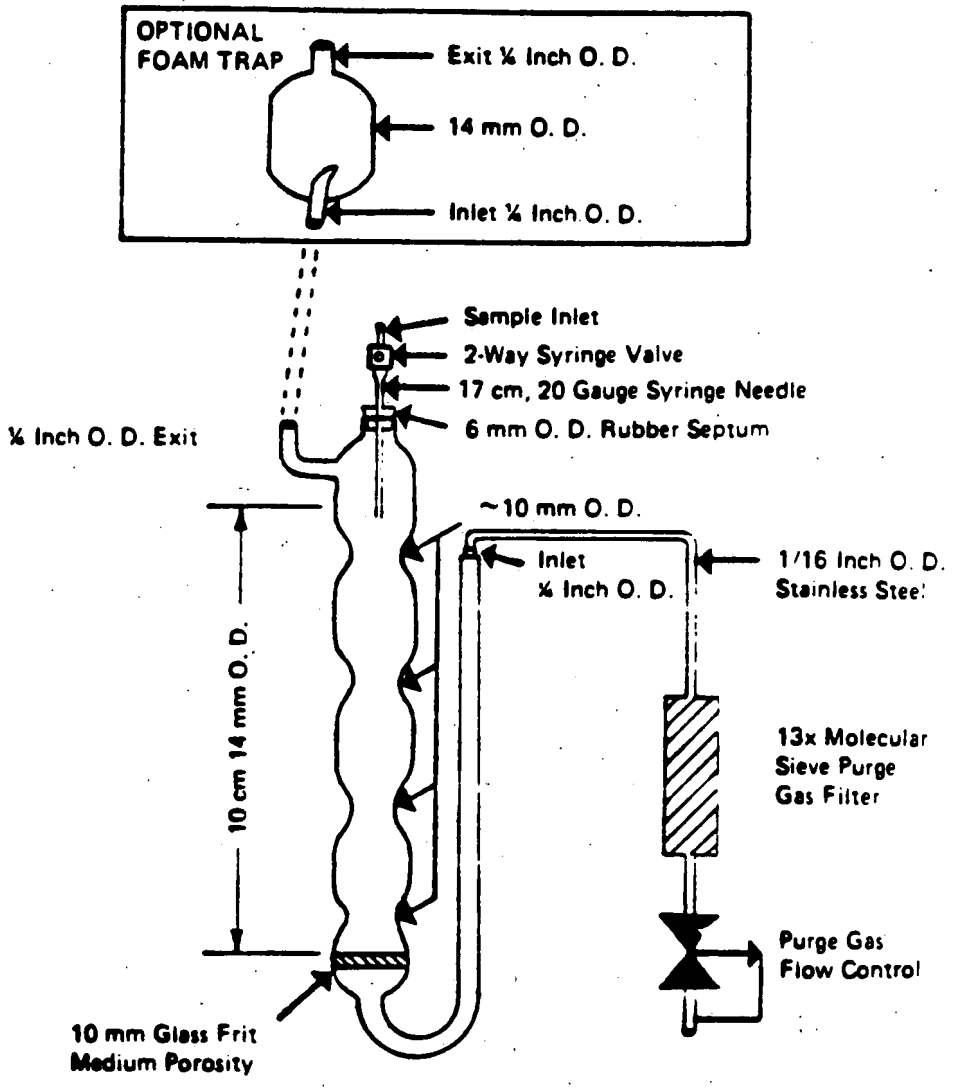


Figure 1. Purging chamber.

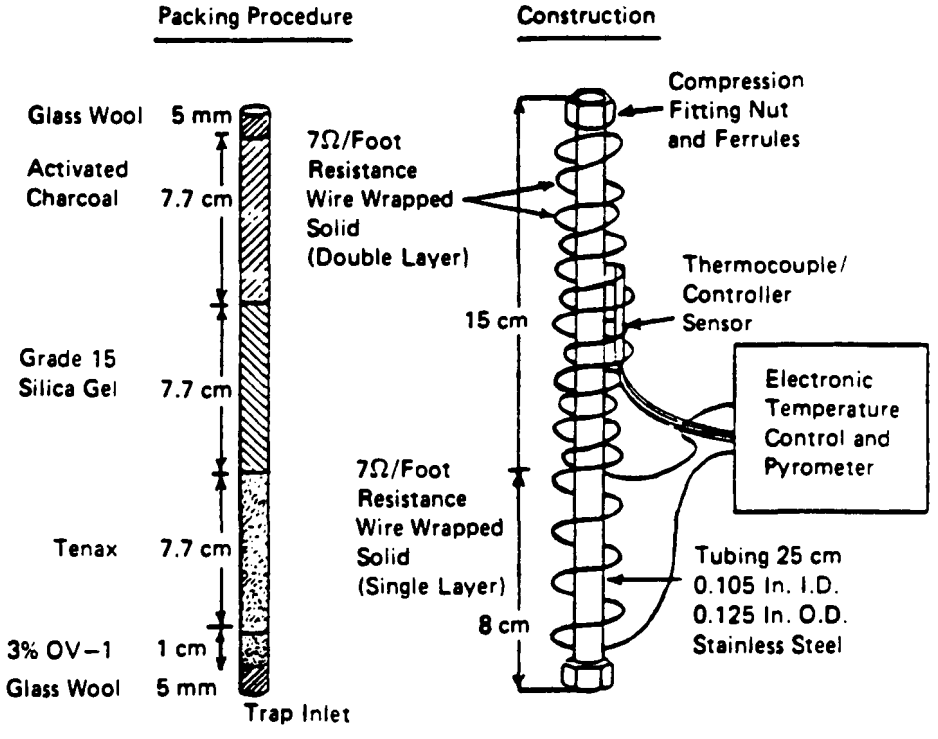


Figure 2. Trap packings and construction for Method 8010.

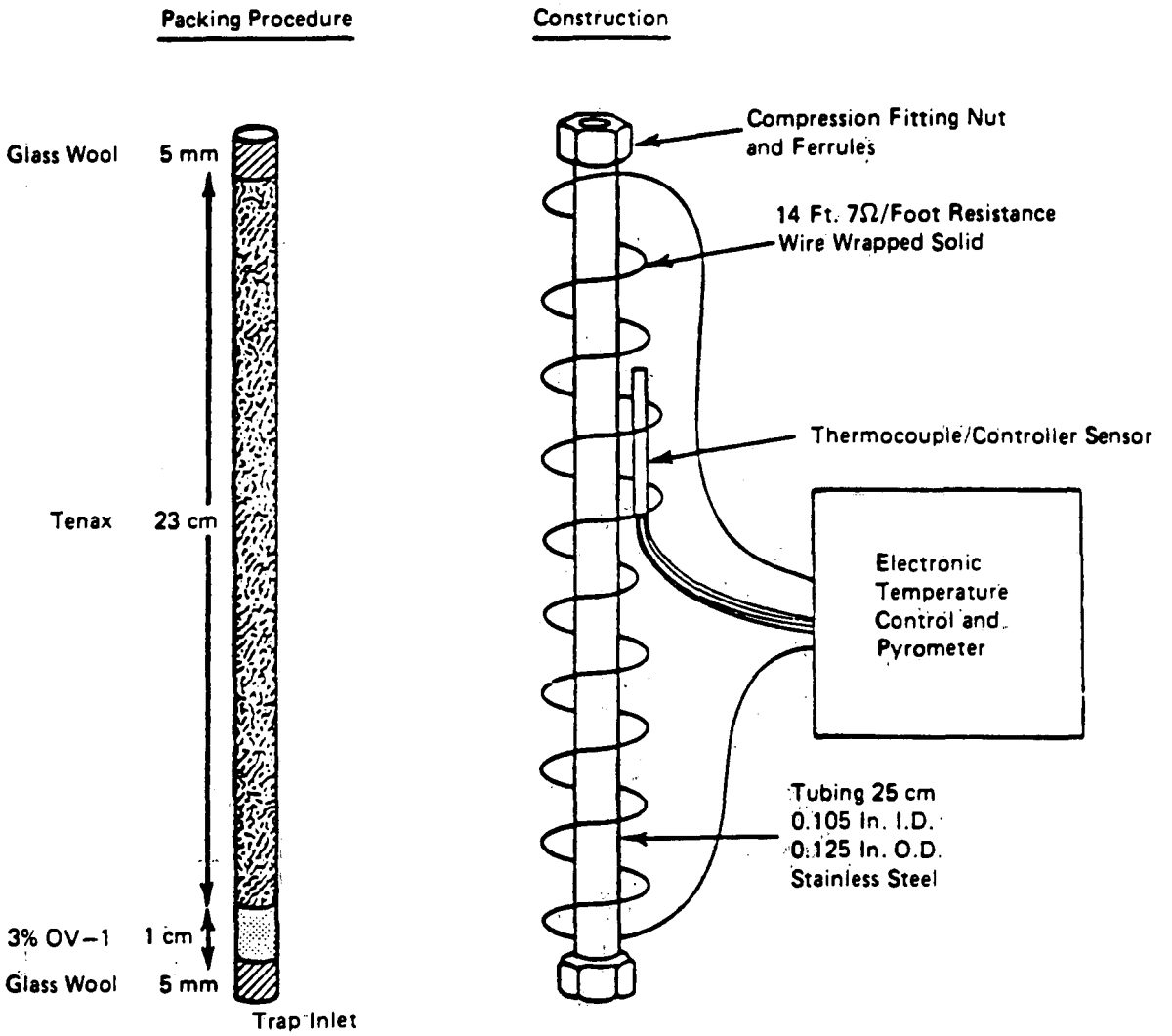


Figure 3. Trap packing and construction for Methods 8020 and 8030.

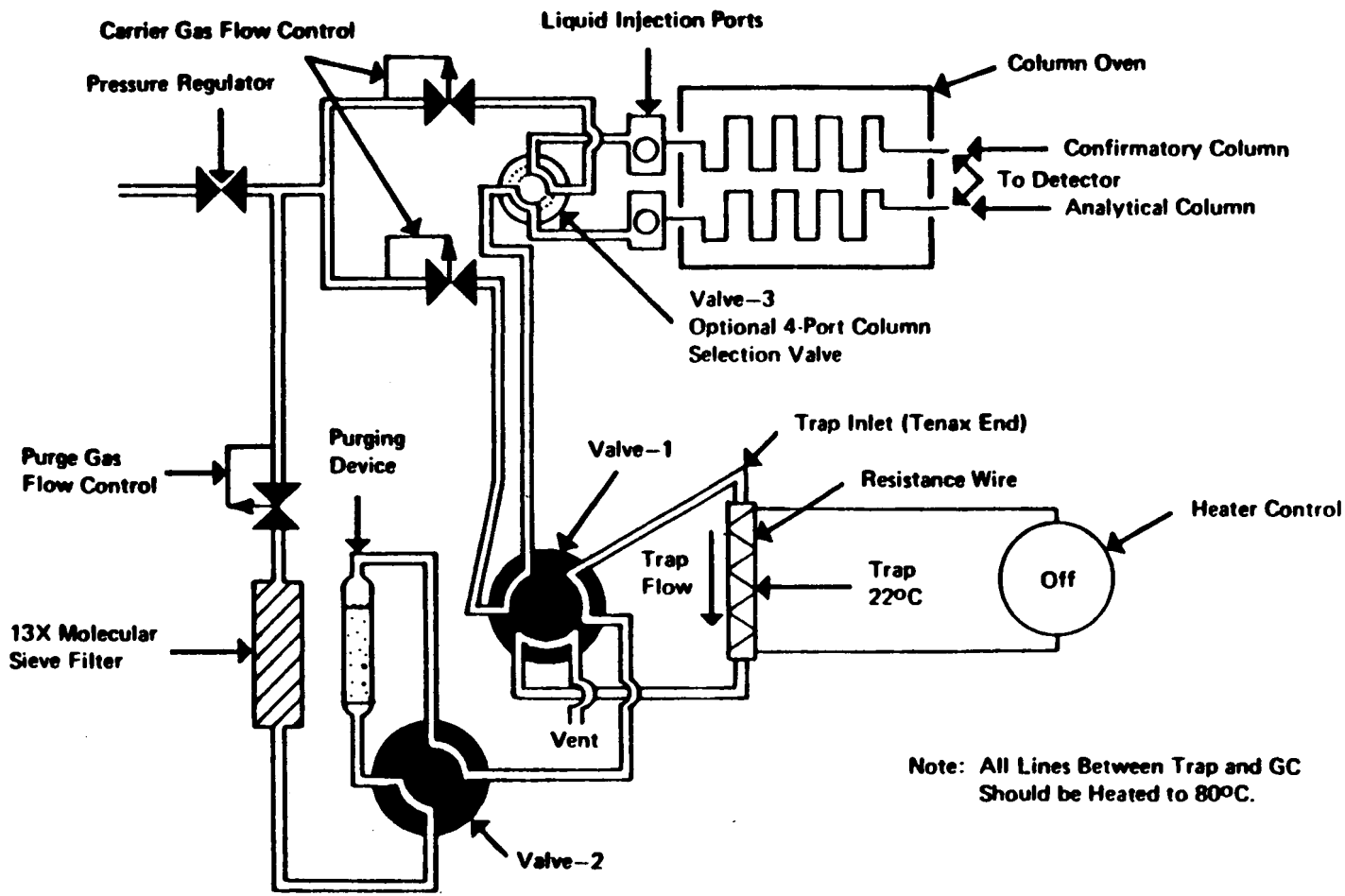


Figure 4. Purge-and-trap system, purge-sorb mode, for Methods 8010, 8020, and 8030.

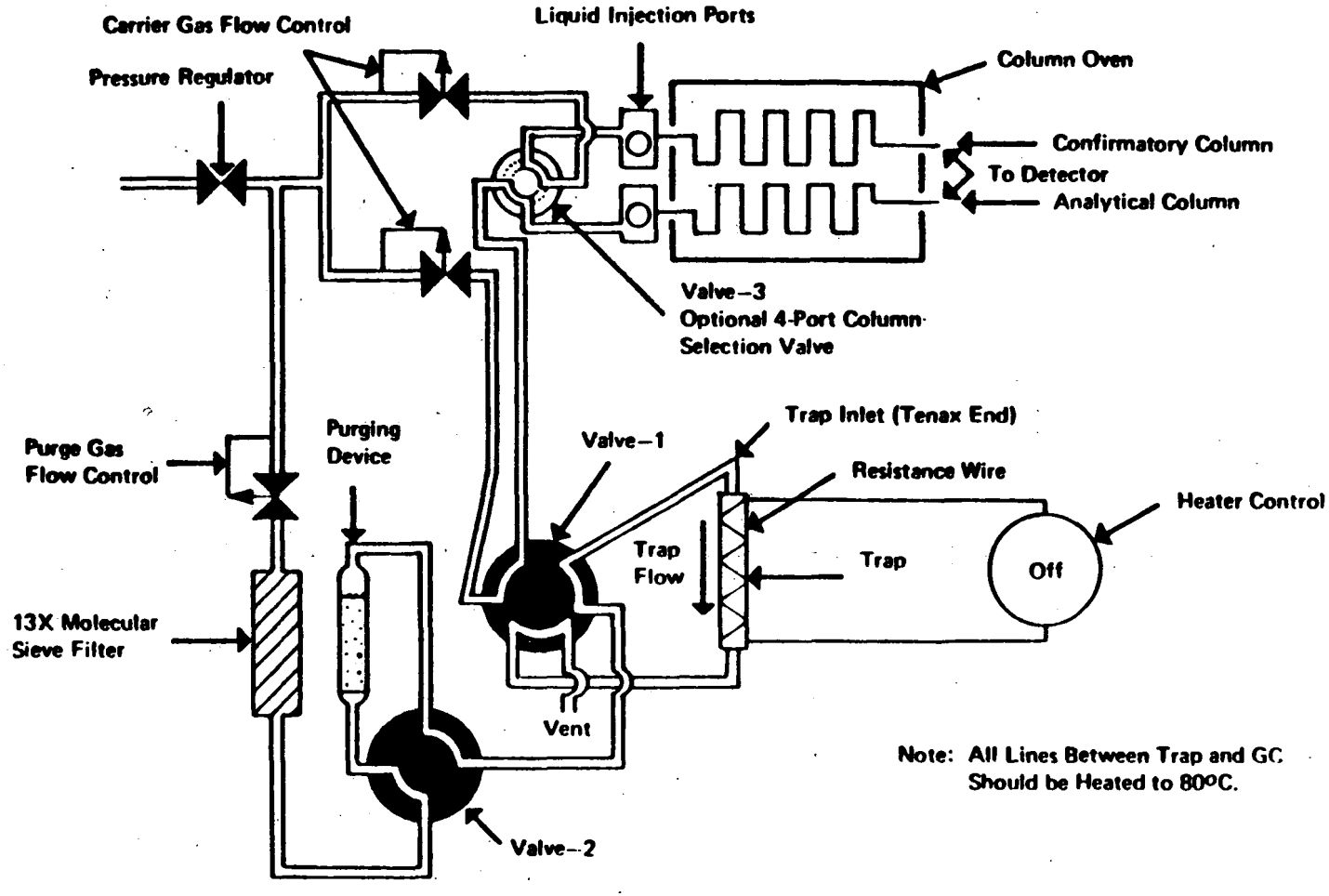


Figure 5. Purge-and-trap system, desorb mode, for Methods 8010, 8020, and 8030.

4.10.5.3 Silica gel: 35/60 mesh, Davison, grade 15 or equivalent.

4.10.5.4 Coconut charcoal: Prepare from Barnebey Cheney, CA-580-26 lot #M-2649, by crushing through 26 mesh screen.

4.11 Heater or heated oil bath: Should be capable of maintaining the purging chamber to within 1°C over a temperature range from ambient to 100°C.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.1.1 Reagent water may be generated by passing trap water through a carbon filter bed containing about 500 g of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

5.1.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the water temperature at 90°C, bubble a contaminant-free inert gas through the water for 1 hr. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

5.2 Methanol: Pesticide quality or equivalent. Store away from other solvents.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Initial calibration: Prior to using this introduction technique for any GC method, the system must be calibrated. General calibration procedures are discussed in Method 8000, Section 7.4, while the specific determinative methods and Method 3500 give details on preparation of standards.

7.1.1 Assemble a purge-and-trap device that meets the specification in Section 4.10. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, condition the trap daily for 10 min while backflushing at 180°C with the column at 220°C.

7.1.2 Connect the purge-and-trap device to a gas chromatograph.

7.1.3 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device. Add 5.0 mL of reagent water to the purging device. The reagent water is added to the purging device using a 5-mL glass syringe fitted with a 15-cm 20-gauge needle. The needle is inserted through the sample inlet shown in Figure 1. The internal diameter of the 14-gauge needle that forms the sample inlet will permit insertion of the 20-gauge needle. Next, using a 10-uL or 25-uL microsyringe equipped with a long needle (Paragraph 4.1), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards. Add the aliquot of calibration solution directly to the reagent water in the purging device by inserting the needle through the sample inlet. When discharging the contents of the microsyringe, be sure that the end of the syringe needle is well beneath the surface of the reagent water. Similarly, add 10 uL of the internal standard solution. Close the 2-way syringe valve at the sample inlet.

7.1.4 Carry out the purge-and-trap analysis procedure using the specific conditions given in Table 1.

7.1.5 Calculate response factors or calibration factors for each analyte of interest using the procedure described in Method 8000, Section 7.4.

7.1.6 The average RF must be calculated for each compound. A system performance check should be made before this calibration curve is used. If the purge-and-trap procedure is used with Method 8010, the following five compounds are checked for a minimum average response factor: chloromethane; 1,1-dichloroethane; bromoform; 1,1,2,2-tetrachloroethane; and chlorobenzene. The minimum acceptable average RF for these compounds should be 0.300 (0.250 for bromoform). These compounds typically have RFs of 0.4-0.6 and are used to check compound instability and check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

7.1.6.1 Chloromethane: This compound is the most likely compound to be lost if the purge flow is too fast.

7.1.6.2 Bromoform: This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response.

7.1.6.3 Tetrachloroethane and 1,1-dichloroethane: These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2 On-going calibration: Refer to Method 8000, Sections 7.4.2.3 and 7.4.3.4 for details on continuing calibration.

TABLE 1. PURGE-AND-TRAP OPERATING PARAMETERS

	Analysis Method			
	8010	8015	8020	8030
Purge gas	Nitrogen or Helium	Nitrogen or Helium	Nitrogen or Helium	Nitrogen or Helium
Purge gas flow rate (mL/min)	40	20	40	20
Purge time (min)	11.0 ± 0.1	15.0 ± 0.1	12.0 ± 0.1	15.0 ± 0.1
Purge temperature (°C)	Ambient	85 ± 2	Ambient	85 ± 2
Desorb temperature (°C)	180	180	180	180
Backflush inert gas flow (mL/min)	20-60	20-60	20-60	20-60
Desorb time (min)	4	1.5	4	1.5

7.3 Sample preparation:

7.3.1 **Water samples:**

7.3.1.1 Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary and will prevent contamination of the purge-and-trap system. Two screening techniques that can be utilized are: the use of an automated headspace sampler (modified Method 3810), interfaced to a gas chromatograph (GC), equipped with a photo ionization detector (PID), in series with an electrolytic conductivity detector (ECD); and extraction of the sample with hexadecane (Method 3820) and analysis of the extract on a GC with a FID and/or an ECD.

7.3.1.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.3.1.3 Assemble the purge-and-trap device. The operating conditions for the GC are given in Section 7.0 of the specific determinative method to be employed.

7.3.1.4 Daily GC calibration criteria must be met (Method 8000, Section 7.4) before analyzing samples.

7.3.1.5 Adjust the purge gas flow rate (nitrogen or helium) to that shown in Table 1, on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response.

7.3.1.6 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hr. Care must be taken to prevent air from leaking into the syringe.

7.3.1.7 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

7.3.1.7.1 Dilutions may be made in volumetric flasks (10-mL to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.3.1.7.2 Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this quantity of reagent water to the flask.

7.3.1.7.3 Inject the proper aliquot of samples from the syringe prepared in Paragraph 7.3.1.5 into the flask. Aliquots of less than 1-mL are not recommended. Dilute the sample to the mark with reagent water. Cap the flask, invert, and shake three times. Repeat the above procedure for additional dilutions.

7.3.1.7.4 Fill a 5-mL syringe with the diluted sample as in Paragraph 7.3.1.5.

7.3.1.8 Add 10.0 uL of surrogate spiking solution (found in each determinative method, Section 5.0) and, if applicable, 10 uL of internal standard spiking solution through the valve bore of the syringe; then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. Matrix spiking solutions, if indicated, should be added (10 uL) to the sample at this time.

7.3.1.9 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

7.3.1.10 Close both valves and purge the sample for the time and at the temperature specified in Table 1.

7.3.1.11 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C while backflushing the trap with inert gas between 20 and 60 mL/min for the time specified in Table 1.

7.3.1.12 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5-mL flushes of reagent water (or methanol followed by reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

7.3.1.13 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 sec; then close the syringe valve on the purging device to begin gas flow

through the trap. The trap temperature should be maintained at 180°C for Methods 8010 and 8020, and 210°C for Methods 8015 and 8030. Trap temperatures up to 220°C may be employed; however, the higher temperature will shorten the useful life of the trap. After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

7.3.1.14 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample is analyzed that has saturated response from a compound, this analysis must be followed by a blank reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

7.3.1.15 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Proceed to Method 8000 and the specific determinative method for details on calculating analyte response.

7.3.2 **Water-miscible liquids:**

7.3.2.1 Water-miscible liquids are analyzed as water samples after first diluting them at least 50-fold with reagent water.

7.3.2.2 Initial and serial dilutions can be prepared by pipetting 2 mL of the sample to a 100-mL volumetric flask and diluting to volume with reagent water. Transfer immediately to a 5-mL gas-tight syringe.

7.3.2.3 Alternatively, prepare dilutions directly in a 5-mL syringe filled with reagent water by adding at least 20 uL, but not more than 100-uL of liquid sample. The sample is ready for addition of surrogate and, if applicable, internal and matrix spiking standards.

7.3.3 **Sediment/soil and waste samples:** It is highly recommended that all samples of this type be screened prior to the purge-and-trap GC analysis. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and-trap system, and require extensive cleanup and instrument downtime. See Paragraph 7.3.1.1 for recommended screening techniques. Use the screening data to determine whether to use the low-level method (0.005-1 mg/kg) or the high-level method (>1 mg/kg).

7.3.3.1 Low-level method: This is designed for samples containing individual purgeable compounds of <1 mg/kg. It is limited to sediment/soil samples and waste that is of a similar consistency (granular and porous). The low-level method is based on

purging a heated sediment/soil sample mixed with reagent water containing the surrogate and, if applicable, internal and matrix spiking standards. Analyze all reagent blanks and standards under the same conditions as the samples.

7.3.3.1.1 Use a 5-g sample if the expected concentration is <0.1 mg/kg or a 1-g sample for expected concentrations between 0.1 and 1 mg/kg.

7.3.3.1.2 The GC system should be set up as in Section 7.0 of the specific determinative method. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and samples. A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed with the low-level method. Follow the initial and daily calibration instructions, except for the addition of a 40°C purge temperature for Methods 8010 and 8020.

7.3.3.1.3 Remove the plunger from a 5-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5.0 mL. Add 10 uL each of surrogate spiking solution and internal standard solution to the syringe through the valve. (Surrogate spiking solution and internal standard solution may be mixed together.) Matrix spiking solutions, if indicated, should be added (10 uL) to the sample at this time.

7.3.3.1.4 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount determined in Paragraph 7.3.3.1.1 into a tared purge device. Note and record the actual weight to the nearest 0.1 g.

7.3.3.1.5 In certain cases, sample results are desired based on a dry-weight basis. When such data is desired, a portion of sample for moisture determination should be weighed out at the same time as the portion used for analytical determination. Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\frac{\text{g of sample - g of dry sample}}{\text{g of sample}} \times 100 = \% \text{ moisture}$$

7.3.3.1.6 Add the spiked reagent water to the purge device, which contains the weighed amount of sample, and connect the device to the purge-and-trap system.

NOTE: Prior to the attachment of the purge device, steps 7.3.3.1.4 and 7.3.3.1.6 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

7.3.3.1.7 Heat the sample to 40°C ± 1°C (Methods 8010 and 8020) or to 85°C ± 2°C (Methods 8015 and 8030) and purge the sample for the time shown in Table 1.

7.3.3.1.8 Proceed with the analysis as outlined in Paragraphs 7.3.1.11-7.3.1.15. Use 5 mL of the same reagent water as in the reagent blank. If saturated peaks occurred or would occur if a 1-g sample were analyzed, the high-level method must be followed.

7.3.3.2 High-level method: The method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. An aliquot of the extract is added to reagent water containing surrogate and, if applicable, internal and matrix spiking standards. This is purged at the temperatures indicated in Table 1. All samples with an expected concentration of >1.0 mg/kg should be analyzed by this method.

7.3.3.2.1 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. For sediment/soil and waste that are insoluble in methanol, weigh 4 g (wet weight) of sample into a tared 20-mL vial. Use a top-loading balance. Note and record the actual weight to 0.1 gram and determine the percent moisture of the sample using the procedure in Paragraph 7.3.3.1.5. For waste that is soluble in methanol, weigh 1 g (wet weight) into a tared scintillation vial or culture tube or a 10-mL volumetric flask. (If a vial or tube is used, it must be calibrated prior to use. Pipet 10.0 mL of methanol into the vial and mark the bottom of the meniscus. Discard this solvent.)

7.3.3.2.2 Quickly add 9.0 mL of methanol; then add 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 min.

NOTE: Steps 7.3.3.2.1 and 7.3.3.2.2 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.3.3.2.3 Pipet approximately 1 mL of the extract to a GC vial for storage, using a disposable pipet. The remainder may be disposed of. Transfer approximately 1 mL of reagent methanol to a separate GC vial for use as the method blank for each set of samples. These extracts may be stored at 4°C in the dark, prior to analysis.

7.3.3.2.4 The GC system should be set up as in Section 7.0 of the specific determinative method. This should be done prior to the addition of the methanol extract to reagent water.

7.3.3.2.5 Table 2 can be used to determine the volume of methanol extract to add to the 5 mL of reagent water for analysis. If a screening procedure was followed, use the estimated concentration to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low-level analysis to determine the appropriate volume. If the sample was submitted as a high-level sample, start with 100 uL. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.3.3.2.6 Remove the plunger from a 5.0-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of standards. Add 10 uL of internal standard solution. Also add the volume of methanol extract determined in Paragraph 7.3.3.2.5 and a volume of methanol solvent to total 100 uL (excluding methanol in standards).

7.3.3.2.7 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the water/methanol sample into the purging chamber.

7.3.3.2.8 Proceed with the analysis as outlined in the specific determinative method. Analyze all reagent blanks on the same instrument as that used for the samples. The standards and blanks should also contain 100 uL of methanol to simulate the sample conditions.

7.3.3.2.9 For a matrix spike in the high-level sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution and 1.0 mL of matrix spike solution. Add a 100-uL aliquot of this extract to 5 mL of water for purging (as per Paragraph 7.3.3.2.6).

TABLE 2. QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH-LEVEL SOILS/SEDIMENTS

Approximate Concentration Range	Volume of Methanol Extract[a]
500-10,000 ug/kg	100 uL
1,000-20,000 ug/kg	50 uL
5,000-100,000 ug/kg	10 uL
25,000-500,000 ug/kg	100 uL of 1/50 dilution [b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a]The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of methanol is necessary to maintain a volume of 100 uL added to the syringe.

[b]Dilute an aliquot of the methanol extract and then take 100 uL for analysis.

7.4 Sample analysis:

7.4.1 The samples prepared by this method may be analyzed by Methods 8010, 8015, 8020, 8030, and 8240. Refer to these methods for appropriate analysis conditions.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3500 for sample preparation procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of a reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

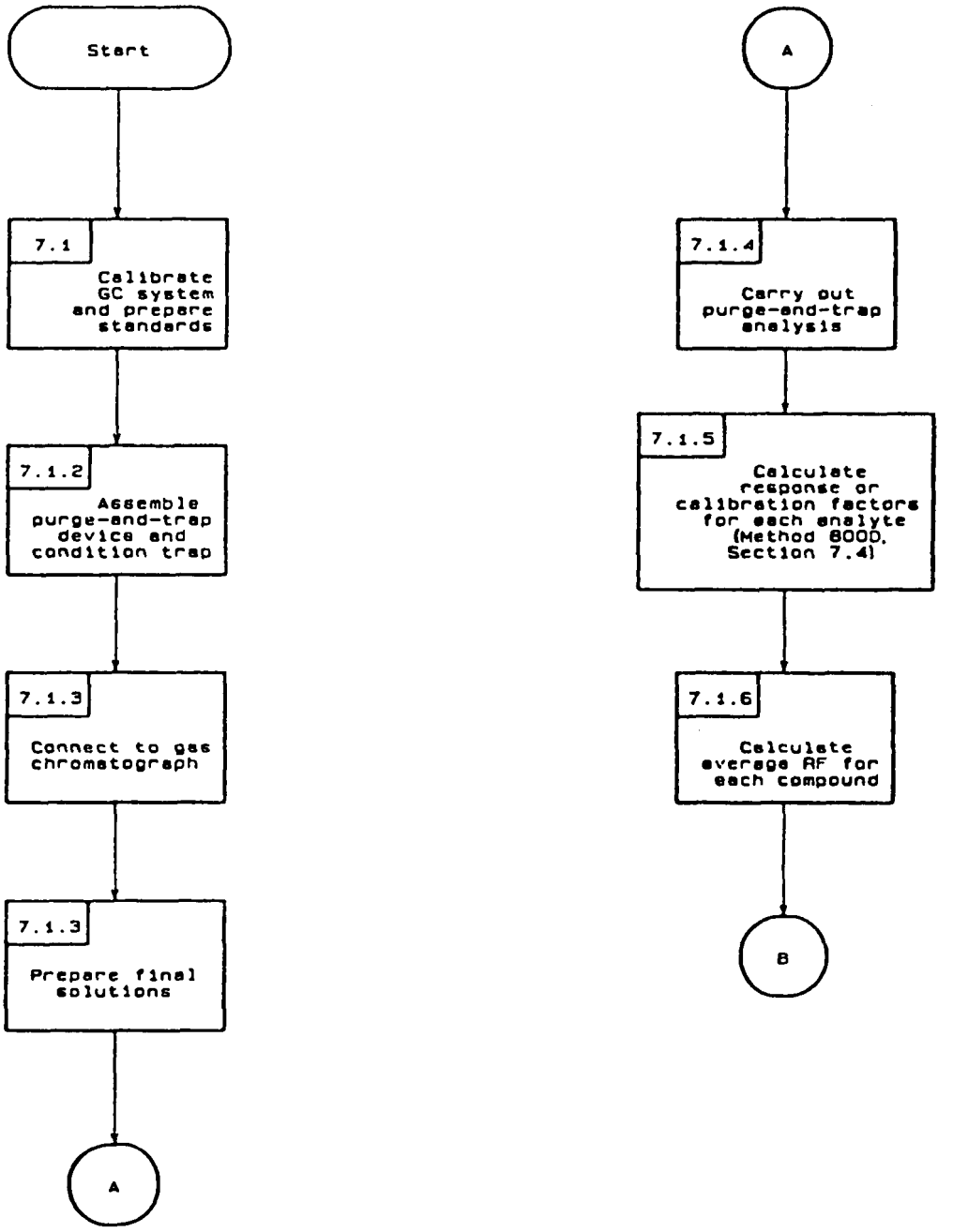
8.3 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified samples do not indicate sufficient sensitivity to detect <1 ug/g of the analytes in the sample, then the sensitivity of the instrument should be increased, or the sample should be subjected to additional cleanup.

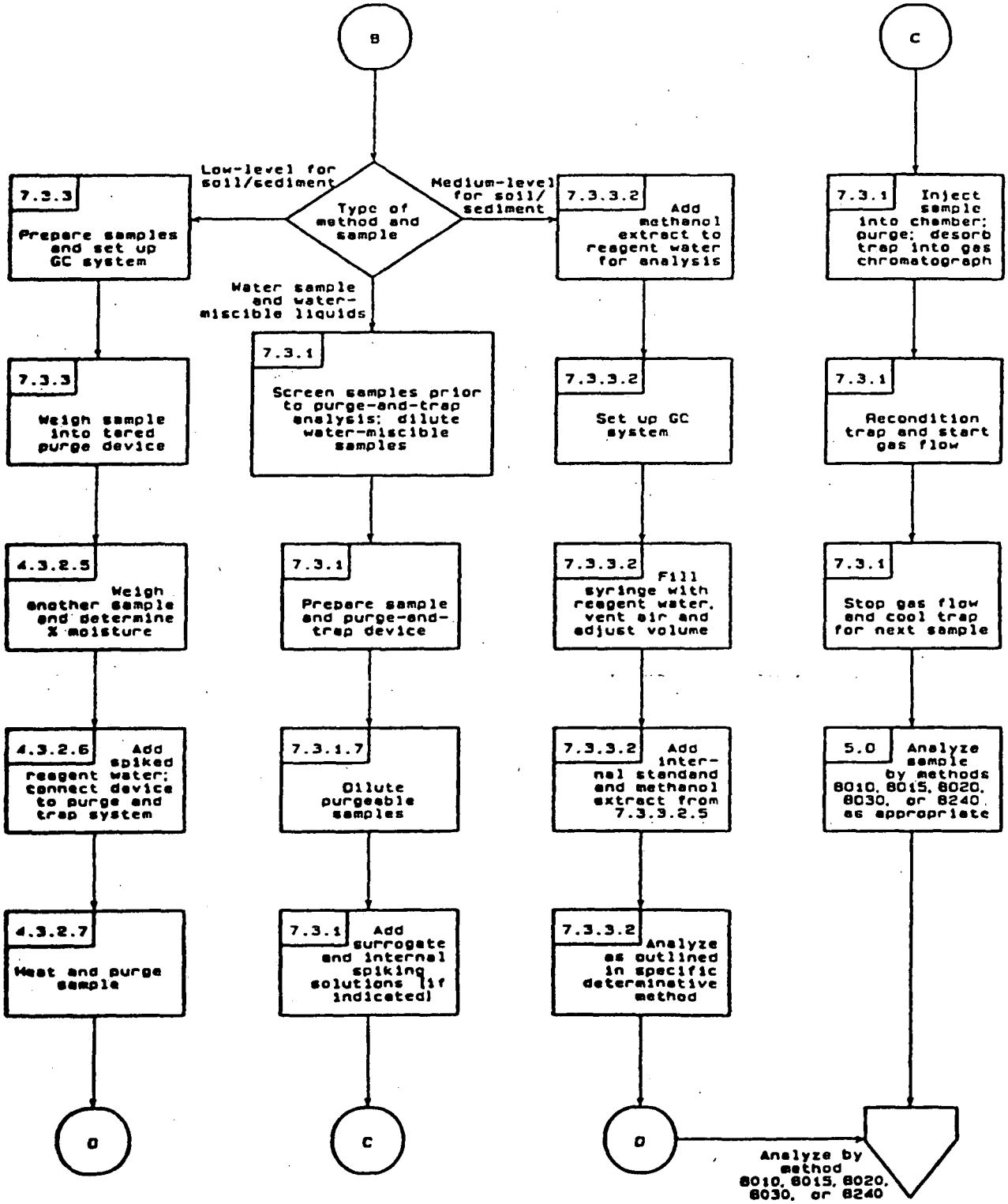
9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.


Start
7.1
Calibrate GC system and prepare standards
7.1.2
Assemble purge-and-trap device and condition trap
7.1.3
Connect to gas chromatograph
7.1.3
Prepare final solutions
A
A
7.1.4
Carry out purge-and-trap analysis
7.1.5
Calculate response or calibration factors for each analyte (Method 8000, Section 7.4)
7.1.6
Calculate average RF for each compound
B


B
C
Type of method and sample
Low-level for soil/sediment
Medium-level for soil/ sediment
Water sample and water-miscible liquids
7.3.3 Prepare samples and set up GC system
7.3.3.2 Add methanol extract to reagent water for analysis
7.3.1 Inject sample into chamber; purge; desorb trap into gas chromatograph
7.3.3 Weigh sample into tared purge device
7.3.1 Screen samples prior to purge-and-trap analysis; dilute water-miscible samples
7.3.3.2 Set up GC system
7.3.1 Recondition trap and start gas flow
4.3.2.5 Weigh another sample and determine % moisture
7.3.1 Prepare sample and purge-and-trap device
7.3.3.2 Fill syringe with reagent water, vent air and adjust volume
7.3.1 Stop gas flow and cool trap for next sample
4.3.2.6 Add spiked reagent water; connect device to purge and trap system
7.3.1.7 Dilute purgeable samples
7.3.3.2 Add internal standard and methanol extract from 7.3.3.2.5
5.0 Analyze sample by methods 8010, 8015, 8020, 8030, or 8240, as appropriate
4.3.2.7 Heat and purge sample
7.3.1 Add surrogate and internal spiking solutions (if indicated)
7.3.3.2 Analyze as outlined in specific determinative method
D
C
D
Analyze by method 8010, 8015, 8020, 8030, or 8240

METHOD 5040

PROTOCOL FOR ANALYSIS OF SORBENT CARTRIDGES FROM VOLATILE ORGANIC SAMPLING TRAIN

1.0 SCOPE AND APPLICATION

1.1 Method 5040 was formerly Method 3720 in the Second Edition of this manual.

1.2 This method covers the determination of volatile principal organic hazardous constituents (POHCs), collected on Tenax and Tenax/charcoal sorbent cartridges using a volatile organic sampling train, VOST (1). Much of the description for purge-and-trap GC/MS analysis is described in Method 8240 of this chapter. Because the majority of gas streams sampled using VOST will contain a high concentration of water, the analytical method is based on the quantitative thermal desorption of volatile POHCs from the Tenax and Tenax/charcoal traps and analysis by purge-and-trap GC/MS. For the purposes of definition, volatile POHCs are those POHCs with boiling points less than 100°C.

1.3 This method is applicable to the analysis of Tenax and Tenax/charcoal cartridges used to collect volatile POHCs from wet stack gas effluents from hazardous waste incinerators.

1.4 The sensitivity of the analytical method for a particular volatile POHC depends on the level of interferences and the presence of detectable levels of volatile POHCs in blanks. The desired target detection limit of the analytical method is 0.1 ng/L (20 ng on a single pair of traps) for a particular volatile POHC desorbed from either a single pair of Tenax and Tenax/charcoal cartridges or by thermal desorption of up to six pairs of traps onto a single pair of Tenax and Tenax/charcoal traps. The resulting single pair of traps is then thermally desorbed and analyzed by purge-and-trap GC/MS.

1.5 This method is recommended for use only by experienced mass spectroscopists or under the close supervision of such qualified persons.

2.0 SUMMARY OF METHOD

2.1 A schematic diagram of the analytical system is shown in Figure 1. The contents of the sorbent cartridges are spiked with an internal standard and thermally desorbed for 10 min at 180°C with organic-free nitrogen or helium gas (at a flow rate of 40 mL/min), bubbled through 5 mL of organic-free water, and trapped on an analytical adsorbent trap. After the 10-min desorption, the analytical adsorbent trap is rapidly heated to 180°C, with the carrier gas flow reversed so that the effluent flow from the analytical trap is directed into the GC/MS. The volatile POHCs are separated by temperature-programmed gas chromatography and detected by low-resolution mass spectrometry. The concentrations of volatile POHCs are calculated using the internal standard technique.

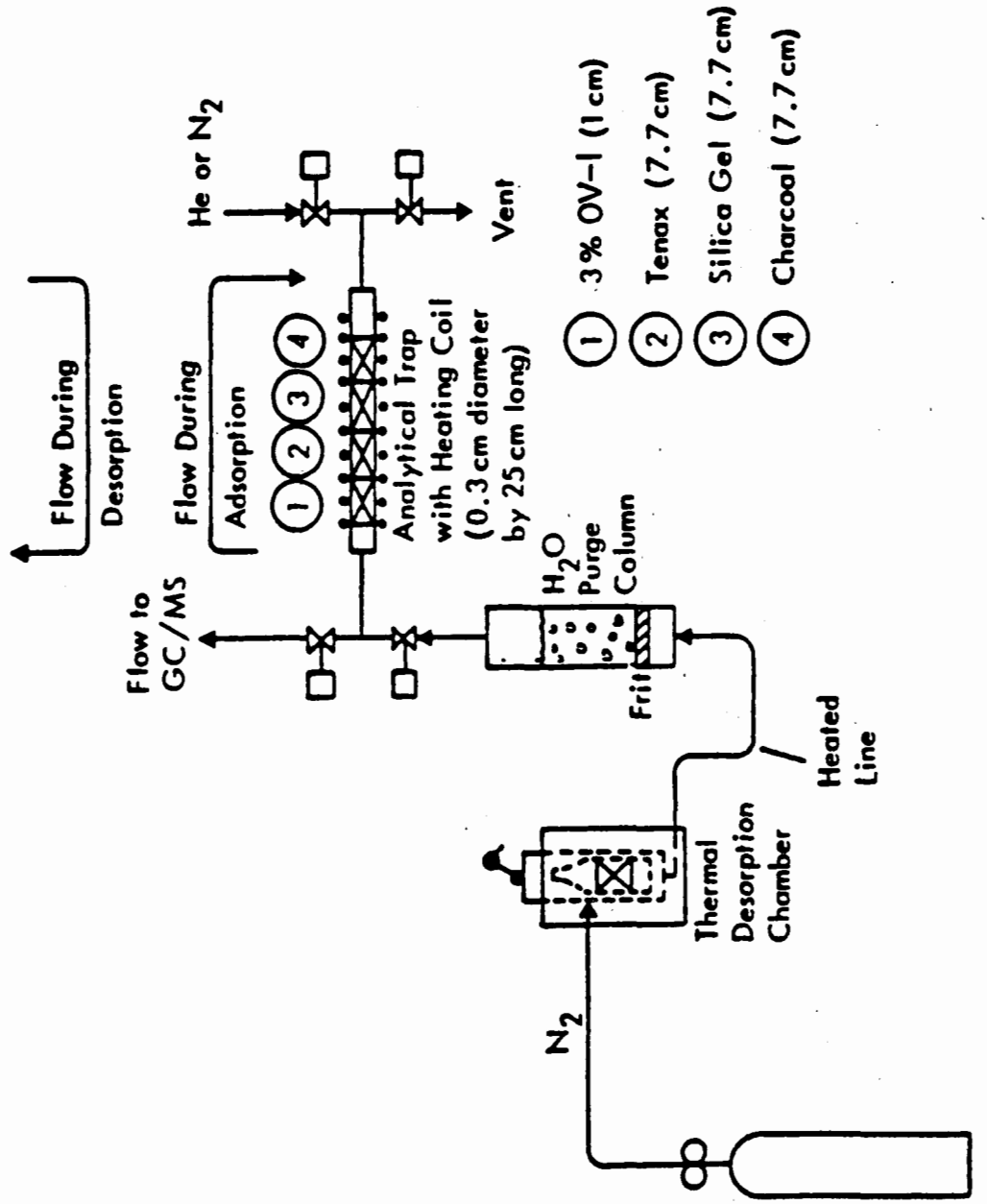


Figure 1. Schematic diagram of trap desorption/analysis system.

3.0 INTERFERENCES

3.1 Refer to Methods 3500 and 8240.

4.0 APPARATUS AND MATERIALS

4.1 Thermal desorption unit:

4.1.1 The thermal desorption unit (for Inside/Inside VOST cartridges, use Supelco "clamshell" heater; for Inside/Outside VOST cartridges, user fabricated unit is required) should be capable of thermally desorbing the sorbent resin tubes. It should also be capable of heating the tubes to 180 ± 10°C with flow of organic-free nitrogen or helium through the tubes.

4.2 Purge-and-trap unit:

4.2.1 The purge-and-trap unit consists of three separate pieces of equipment: the sample purger, trap, and the desorber. It should be capable of meeting all requirements of Method 5030 for analysis of purgeable organic compounds from water.

4.3 GC/MS system: As described in Method 8240.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the parameters of interest.

5.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 450 g of activated carbon (Calgon Corporation, Filtrasorb-300, or equivalent).

5.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

5.1.3 Reagent water may also be prepared by boiling distilled water for 15 min. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for 1 hr. Allow the water to cool to room temperature while continuing to bubble the inert gas through the water. This water should be transferred directly to the purge-and-trap apparatus for use.

5.1.4 Other methods that can be shown to produce organic-free water can be used.

5.2 Analytical trap reagents:

5.2.1 **2,6-Diphenylene oxide polymer:** Tenax (60/80 mesh), chromatographic grade or equivalent.

5.2.2 **Methyl silicone packing:** 3% OV-1 on Chromosorb W (60/80 mesh) or equivalent.

5.2.3 **Silica gel:** Davison Chemical (35/00 mesh), Grade 15, or equivalent.

5.2.4 **Charcoal:** Petroleum-based (SKC Lot 104 or equivalent).

5.3 Stock standard solution:

5.3.1 Stock standard solutions will be prepared from pure standard materials or purchased as certified solutions. The stock standards should be prepared in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be used when the analyst handles high concentrations of such materials.

5.3.2 Fresh stock standards should be prepared weekly for volatile POHCs with boiling points of <35°C. All other standards must be replaced monthly, or sooner if comparison with check standards indicates a problem.

5.4 Secondary dilution standards:

5.4.1 Using stock standard solutions, prepare in methanol secondary dilution standards that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the desorbed calibration standards will bracket the working range of the analytical system.

5.5 4-Bromofluorobenzene (BFB) standard:

5.5.1 Prepare a 25 ng/uL solution of BFB in methanol.

5.6 Deuterated benzene:

5.6.1 Prepare a 25 ng/uL solution of benzene-d_6 in methanol.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to Method 0030, Chapter Ten.

6.2 Sample trains obtained from the VOST should be analyzed within 2-6 weeks of sample collection.

7.0 PROCEDURE

7.1 Assembly of PTD device:

7.1.1 Assemble a purge-and-trap desorption device (PTD) that meets all the requirements of Method 5030 (refer to Figure 1).

7.1.2 Connect the thermal desorption device to the PTD device. Calibrate the PTD-GC/MS system using the internal standard technique.

7.2 Internal standard calibration procedure:

7.2.1 This approach requires the use of deuterated benzene as the internal standard for these analyses. Other internal standards may be proposed for use in certain situations. The important criteria for choosing a particular compound as an internal standard are that it be similar in analytical behavior to the compounds of interest and that it can be demonstrated that the measurement of the internal standard be unaffected by method or matrix interferences. Other internal standards that have been used are d_{10}-ethylbenzene and d_4-1,2-dichloroethane. One adds 50 ng of BFB to all sorbent cartridges (in addition to one or more internal standards) to provide continuous monitoring of the GC/MS performance relative to BFB.

7.2.2 Prepare calibration standards at a minimum of three concentration levels for each analyte of interest.

7.2.3 The calibration standards are prepared by spiking a blank Tenax or Tenax/charcoal trap with a methanolic solution of the calibration standards (including 50 ng of the internal standard, such as deuterated benzene), using the flash evaporation technique. The flash evaporation technique requires filling the needle of a 5.0-uL syringe with clean methanol and drawing air into the syringe to the 1.0-uL mark. This is followed by drawing a methanolic solution of the calibration standards (containing 25 ug/uL of the internal standard) to the 2.0-uL mark. The glass traps should be attached to the injection port of a gas chromatograph while maintaining the injector temperature at 160°C. The carrier gas flow through the traps should be maintained at about 50 mL/min.

7.2.4 After directing the gas flow through the trap, the contents of the syringe should be slowly expelled through the gas chromatograph injection port over about 15 sec. After 25 sec have elapsed, the gas flow through the trap should be shut off, the syringe removed, and the trap analyzed by the PTD-GC/MS procedure outlined in Method 8240. The total flow of gas through the traps during addition of calibration standards to blank cartridges, or internal standards to sample cartridges, should be 25 mL or less.

7.2.5 Analyze each calibration standard for both Tenax and Tenax/charcoal cartridges according to Section 7.3. Tabulate the area response

of the characteristic ions of each analyte against the concentration of the internal standard and calculate response factor (RF) for each compound, using Equation 1.

$$RF = A_S C_{is} / A_{is} C_S \quad (1)$$

where:

A_S = Area of the characteristic ion for the analyte to be measured.

A_{is} = Area of the characteristic ion for the internal standard.

C_{is} = Amount (ng) of the internal standard.

C_S = Amount (ng) of the volatile POHC in calibration standard.

If the RF value over the working range is a constant (<10% RSD), the RF can be assumed to be invariant, and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_S/A_{is} versus RF.

7.2.6 The working calibration curve or RF must be verified on each working day by the measurement of one or more of the calibration standards. If the response varies by more than ±25% for any analyte, a new calibration standard must be prepared and analyzed, for that analyte.

7.3 The schematic of the PTD-GC/MS system is shown in Figure 1. The sample cartridge is placed in the thermal desorption apparatus (for Inside/Inside VOST cartridges, use Supelco "clamshell" heater; for Inside/Outside VOST cartridges, user fabricated unit is required) and desorbed in the purge-and-trap system by heating to 180°C for 10 min at a flow rate of 40 mL/min. The desorbed components pass into the bottom of the water column, are purged from the water, and collected on the analytical adsorbent trap. After the 10-min desorption period, the compounds are desorbed from the analytical adsorbent trap into the GC/MS system according to the procedures described in Method 8240.

7.4 Qualitative identification:

7.4.1 The procedure for qualitative identification of volatile POHCs using this protocol is described in Method 8240.

7.5 Calculations:

7.5.1 When an analyte has been qualitatively identified, quantification should be based on the integrated abundance from the EICP of the primary characteristic ion chosen for that analyte. If the sample produces an interference for the primary characteristic ion, a secondary characteristic ion should be used.

7.5.1.1 Using the internal standard calibration procedure, the amount of analyte in the sample cartridge is calculated using the response factor (RF) determined in Paragraph 7.2.5 and Equation 2.

$$\text{Amount of POHC} = A_S C_{is} / A_{is} RF \quad (2)$$

where:

A_S = Area of the characteristic ion for the analyte to be measured.

A_{is} = Area for the characteristic ion of the internal standard.

C_{is} = Amount (ng) of internal standard.

7.5.1.2 The choice of methods for evaluating data collected using VOST for incinerator trial burns is a regulatory decision. The procedures used extensively by one user are outlined below.

7.5.1.3 The total amount of the POHCs of interest collected on a pair of traps should be summed. These values should then be blank corrected. Guidelines for blank correction of sample cartridges are outlined below.

7.5.1.3.1 After all blanks (field and trip) are analyzed, a paired t-test should be used to determine whether trip blanks are significantly different from field blanks. If no difference is found, then the mean and standard deviation of the combined field and trip blanks for each POHC of interest is calculated.

7.5.1.3.2 If, when using the paired t-test, the field and trip blanks are determined to be different, then the field blank (or the mean of multiple field blanks) associated with a particular run should be used as the blank value for that particular run.

7.5.1.4 Next, for each sample/POHC combination, a determination must be made as to whether a particular sample is significantly different from the associated blank. If the mean of the trip and field blanks is used, then a sample is different from the blank if:

$$(\text{measured sample value}) - (\text{mean blank value}) > (3 \times \text{blank standard deviation})$$

(If an individual field blank is used as the blank value, the above criteria do not apply.) If the sample is determined to be different from the blank according to the above criteria, then the emission value of a particular POHC is blank-corrected by subtracting the mean blank value from the measured sample value.

7.5.1.5 If, according to the above procedures, the sample cannot be distinguished from the blank (i.e., for a given POHC there is a high sample value and high blank value or there is a low sample value and low blank value), the measured sample value is not blank-corrected. In this case, the measured sample value is used to calculate a maximum emission value (and therefore a minimum DRE value) for that particular run.

7.5.1.6 The observation of high concentrations of POHCs of interest in blank cartridges indicates possible residual contamination of the sorbent cartridges prior to shipment to and use at the site. Data that fall in this category (especially data indicating high concentrations of POHCs in blank sorbent cartridges) should be qualified with regard to validity, and blank data should be reported separately. The applicability of data of this type to the determination of DRE is a regulatory decision. Continued observation of high concentrations of POHCs in blank sorbent cartridges indicates that procedures for cleanup, monitoring, shipment, and storage of sorbent cartridges by a particular user be investigated to eliminate this problem.

7.5.1.7 If any internal standard recoveries fall outside the control limits established in Section 8.4, data for all analytes determined for that cartridge(s) must be qualified with the observation.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3500 for sample preparation procedures.

8.2 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of blank Tenax and Tenax/charcoal cartridges spiked with the analytes of interest. The laboratory is required to maintain performance records to define the quality of data that are generated. Ongoing performance checks must be compared with established performance criteria to determine if results are within the expected precision and accuracy limits of the method.

8.2.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable precision and accuracy with this method. This ability is established as described in Paragraph 7.2.

8.2.2 The laboratory must spike all Tenax and Tenax/charcoal cartridges with the internal standard(s) to monitor continuing laboratory performance. This procedure is described in Paragraph 7.2.

8.3 To establish the ability to generate acceptable accuracy and precision, the analyst must spike blank Tenax and Tenax/charcoal cartridges with the analytes of interest at two concentrations in the working range.

8.3.1 The average response factor (R) and the standard deviation (S) for each must be calculated.

8.3.2 The average recovery and standard deviation must fall within the expected range for determination of volatile POHCs using this method. The expected range for recovery of volatile POHCs using this method is 50-150%.

8.4 The analyst must calculate method performance criteria for the internal standard(s).

8.4.1 Calculate upper and lower control limits for method performances using the average area response (A) and standard deviation(s) for internal standard:

Upper Control Limit (UCL) = A + 3S.
Lower Control Limit (LCL) = A - 3S.

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance. The control limits must be replaced by method performance criteria as they become available from the U.S. EPA.

8.5 The laboratory is required to spike all sample cartridges (Tenax and Tenax/charcoal) with internal standard.

8.6 Each day, the analyst must demonstrate through analysis of blank Tenax and Tenax/charcoal cartridges and reagent water that interferences from the analytical system are under control.

8.7 The daily GC/MS performance tests required for this method are described in Method 8240.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

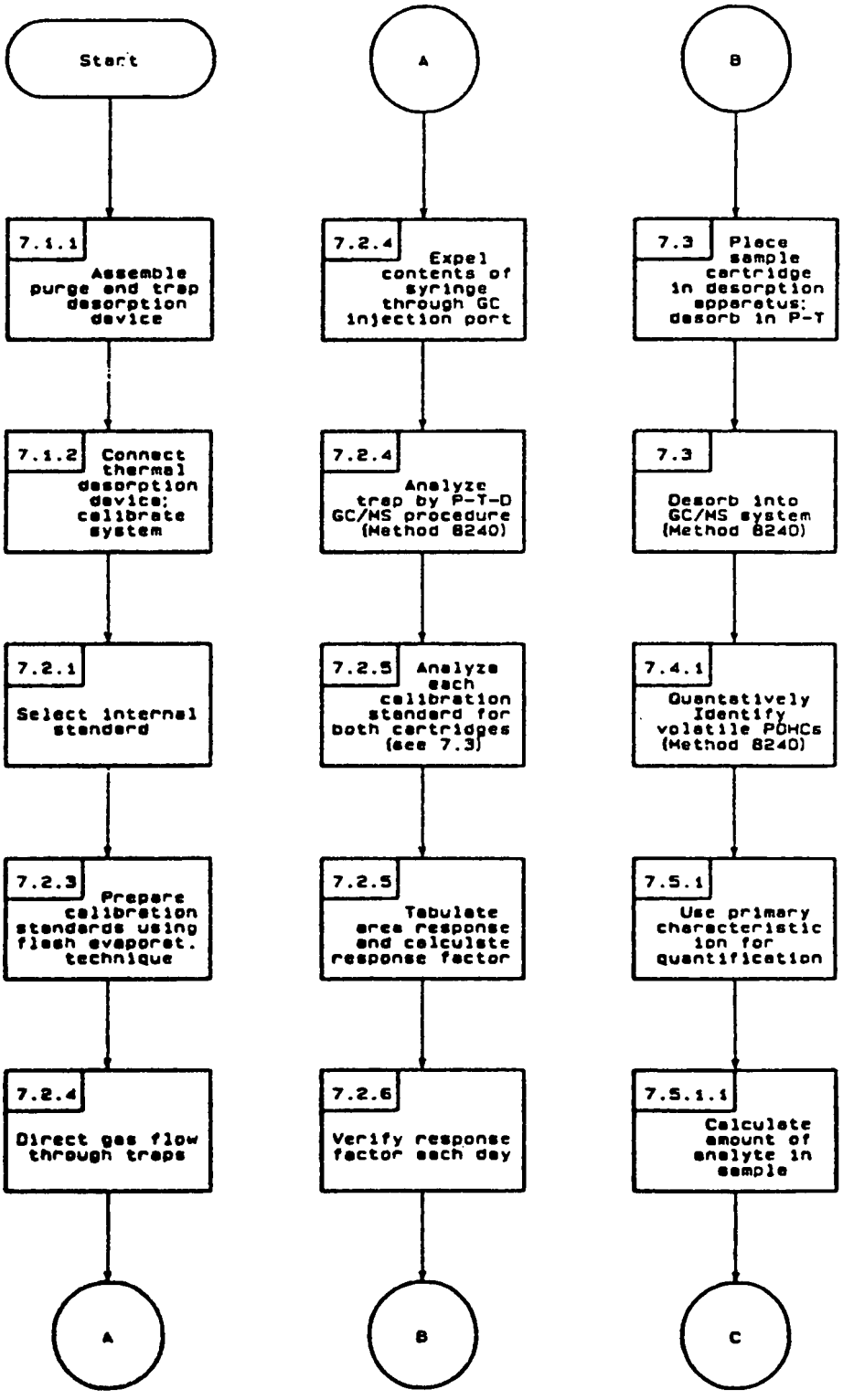
1. Protocol for Collection and Analysis of Volatile POHC's Using VOST. EPA/600/8-84-007, March 1984.

2. Validation of the Volatile Organic Sampling Train (VOST) Protocol. Volumes I and II. EPA/600/4-86-014a, January 1986.

METHOD 5040

PROTOCOL FOR ANALYSIS OF SORBENT CARTRIDGES

FROM VOLATILE ORGANIC SAMPLING TRAIN



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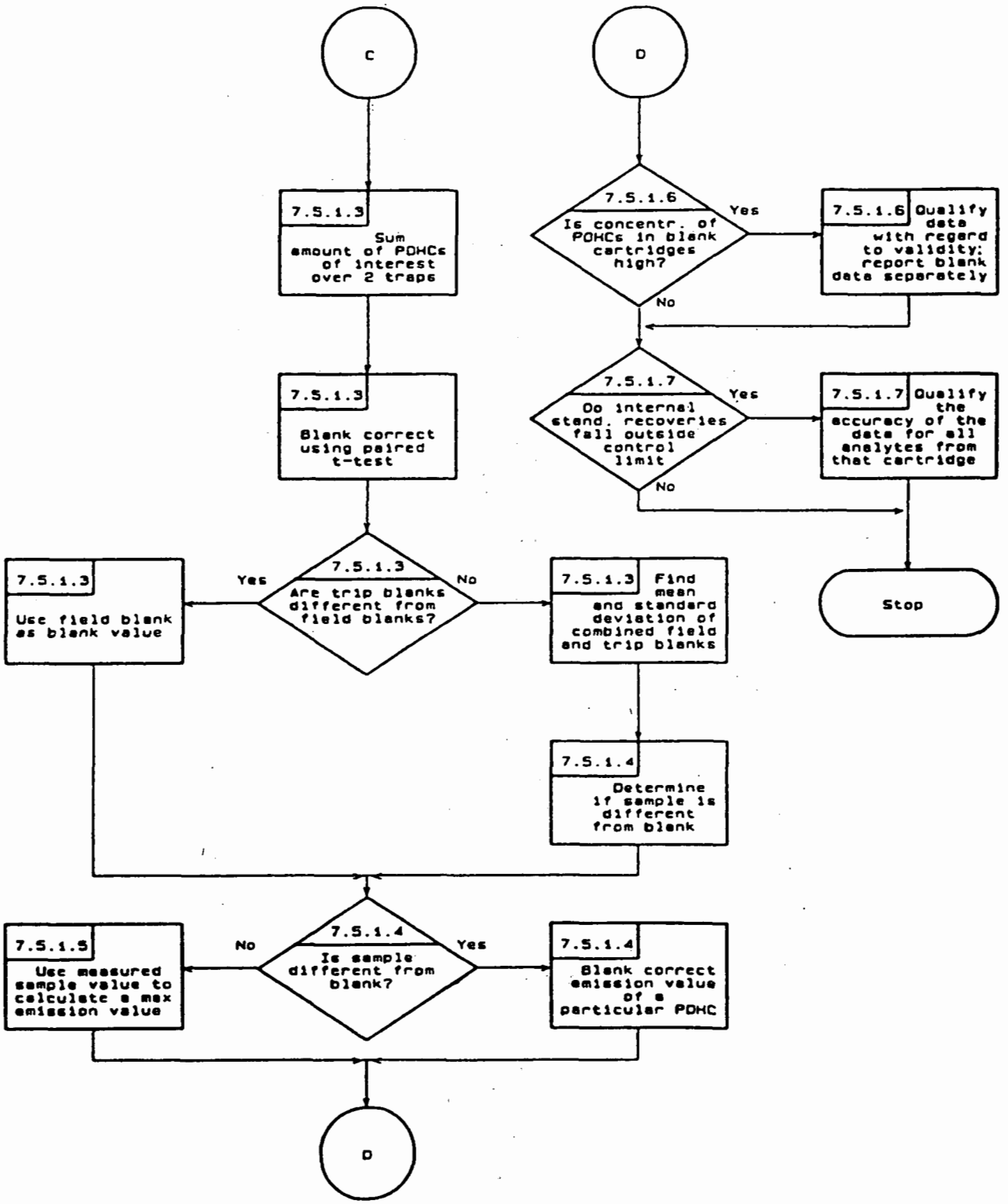

C
D
7.5.1.3
Sum amount of PDHCs of interest over 2 traps
7.5.1.6
Is concentr. of PDHCs in blank cartridges high?
Yes
No
7.5.1.6 Qualify data with regard to validity; report blank data separately
7.5.1.3
Blank correct using paired t-test
7.5.1.7
Do internal stand. recoveries fall outside control limit
Yes
No
7.5.1.7 Qualify the accuracy of the data for all analytes from that cartridge
Stop
7.5.1.3
Are trip blanks different from field blanks?
Yes
No
7.5.1.3
Use field blank as blank value
7.5.1.3 Find mean and standard deviation of combined field and trip blanks
7.5.1.4
Determine if sample is different from blank
7.5.1.4
Is sample different from blank?
No
Yes
7.5.1.5
Use measured sample value to calculate a max emission value
7.5.1.4
Blank correct emission value of a particular PDHC
D

4.2 SAMPLE PREPARATION METHODS

4.2.2 CLEANUP

METHOD 3600

CLEANUP

1.0 SCOPE AND APPLICATION

1.1 General:

1.1.1 Injection of extracts into a gas or liquid chromatograph can cause extraneous peaks, deterioration of peak resolution and column efficiency, and loss of detector sensitivity and can greatly shorten the lifetime of expensive columns. The following techniques have been applied to extract purification: partitioning between immiscible solvents; adsorption chromatography; gel permeation chromatography; chemical destruction of interfering substances with acid, alkali, or oxidizing agents; and distillation. These techniques may be used individually or in various combinations, depending on the extent and nature of the co-extractives.

1.1.2 It is an unusual situation, e.g., with some water samples, when extracts can be directly determined without further treatment. Soil and waste extracts often require a combination of cleanup methods. For example, when analyzing for organochlorine pesticides and PCBs, it may be necessary to use gel permeation chromatography (GPC), to eliminate the high boiling material and a micro alumina or Florisil column to eliminate interferences with the analyte peaks on the GC/ECD.

1.2 Specific:

1.2.1 **Adsorption column chromatography:** Alumina (Methods 3610 and 3611), Florisil (Method 3620), and silica gel (Method 3630) are useful for separating analytes of a relatively narrow polarity range away from extraneous, interfering peaks of a different polarity.

1.2.2 **Acid-base partitioning:** Useful for separating acidic or basic organics from neutral organics. It has been applied to analytes such as the chlorophenoxy herbicides and phenols.

1.2.3 **Gel permeation chromatography** (GPC): The most universal cleanup technique for a broad range of semivolatile organics and pesticides. It is capable of separating high molecular-weight material from the sample analytes. It has been used successfully for all the semivolatile base, neutral, and acid compounds associated with the EPA Priority Pollutant and the Superfund Hazardous Substance Lists. GPC is usually not applicable for eliminating extraneous peaks on a chromatogram which interfere with the analytes of interest.

1.2.4 **Sulfur cleanup:** Useful in eliminating sulfur from sample extracts, which may cause chromatographic interference with analytes of interest.

1.2.5 Table 1 indicates the recommended cleanup techniques for the indicated groups of compounds. This information can also be used as guidance for compounds that are not listed. Compounds that are chemically similar to these groups of compounds should follow a similar elution pattern.

2.0 SUMMARY OF METHOD

2.1 Refer to the specific cleanup method for a summary of the procedure.

3.0 INTERFERENCES

3.1 Analytical interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free of interferences, under the conditions of the analysis, by running laboratory reagent blanks.

3.2 More extensive procedures than those outlined in the methods may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific cleanup method for apparatus and materials needed.

5.0 REAGENTS

5.1 Refer to the specific cleanup method for the reagents needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Prior to using the cleanup procedures, samples should undergo solvent extraction. Chapter Two, Section 2.3.3, may be used as a guide for choosing the appropriate extraction procedure based on the physical composition of the waste and on the analytes of interest in the matrix (see also Method 3500 for a general description of the extraction technique). For some organic liquids, extraction prior to cleanup may not be necessary

7.2 In most cases, the extracted sample is then analyzed by one of the determinative methods available in Section 4.3 of this chapter. If the analytes of interest are not able to be determined due to interferences, cleanup is performed.

TABLE 1. RECOMMENDED CLEANUP TECHNIQUES FOR INDICATED GROUPS OF COMPOUNDS

Analyte Group	Determinative[a] Method	Cleanup Method Option
Phenols	8040	3630[b], 3640, 3650, 8040[c]
Phthalate esters	8060	3610, 3620, 3640
Nitrosamines	8070	3610, 3620, 3640
Organochlorine pesticides & PCBs	8080	3620, 3640, 3660
Nitroaromatics and cyclic ketones	8090	3620, 3640
Polynuclear aromatic hydrocarbons	8100	3611, 3630, 3640
Chlorinated hydrocarbons	8120	3620, 3640
Organophosphorous pesticides	8140	3620, 3640
Chlorinated herbicides	8150	8150[d]
Priority pollutant semivolatiles	8250, 8270	3640, 3650, 3660
Petroleum waste	8250, 8270	3611, 3650

[a] The GC/MS Methods, 8250 and 8270, are also appropriate determinative methods for all analyte groups, unless lower detection limits are required.

[b] Cleanup applicable to derivatized phenols.

[c] Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered using GC/FID.

[d] Method 8150 incorporates an acid-base cleanup step as an integral part of the method.

7.3 Many of the determinative methods specify cleanup methods that should be used when determining particular analytes; e.g., Method 8060 (gas chromatography of phthalate esters) recommends using either Method 3610 (Alumina column cleanup) or Method 3620 (Florisil column cleanup) if interferences prevent analysis. However, the experience of the analyst may prove invaluable in determining which cleanup methods are needed. As indicated in Section 1.0 of this method, many matrices may require a combination of cleanup procedures in order to ensure proper analytical determinations.

7.4 Guidance for cleanup is specified in each of the methods that follow. The amount of extract cleanup required prior to the final determination depends on the selectivity of both the extraction procedure and the determinative method and the required detection limit.

7.5 Following cleanup, the sample is concentrated to whatever volume is required in the determinative method. Analysis follows as specified in the determinative procedure (Section 4.3 of this chapter).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 The analyst must demonstrate that the compounds of interest are being quantitatively recovered by the cleanup technique before the cleanup is applied to actual samples.

8.2 For sample extracts that are cleaned up, the associated quality control samples (e.g., spikes, blanks, and duplicates) must also be processed through the same cleanup procedure.

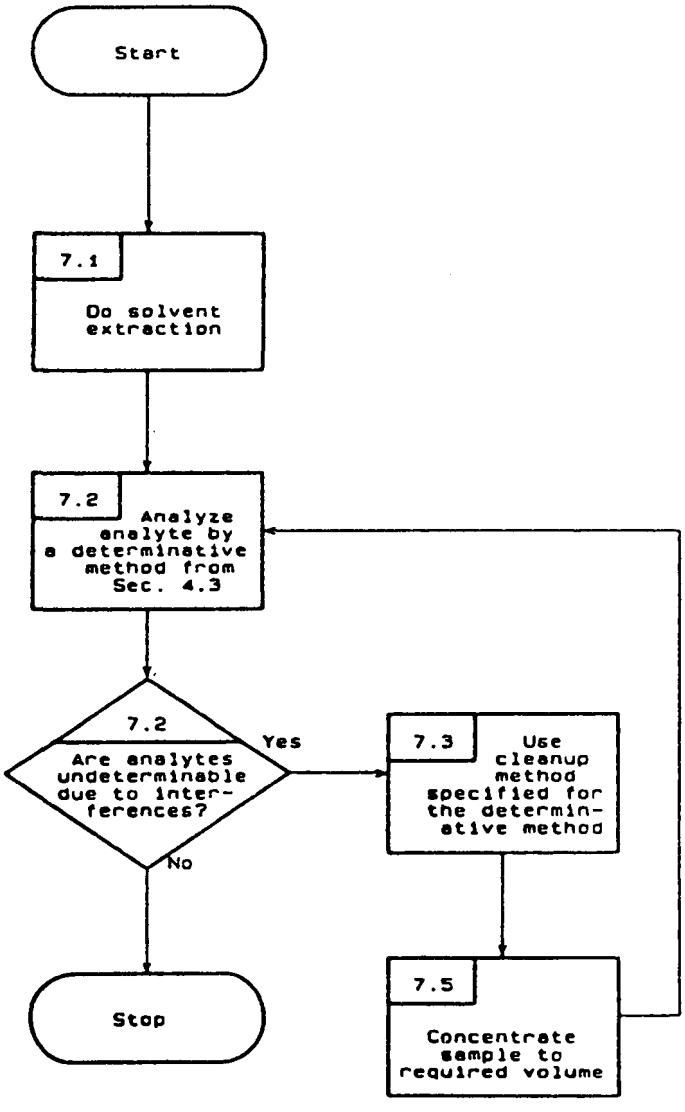
8.3 The analysis using each determinative method (GC, GC/MS, HPLC) specifies instrument calibration procedures using stock standards. It is recommended that cleanup also be performed on a series of the same type of standards to validate chromatographic elution patterns for the compounds of interest and to verify the absence of interferences from reagents.

9.0 METHOD PERFORMANCE

9.1 Refer to the specific cleanup method for performance data.

10.0 REFERENCES

10.1 Refer to the specific cleanup method.


Start
7.1
Do solvent extraction
7.2
Analyze analyte by a determinative method from Sec. 4.3
7.2
Are analytes undeterminable due to interferences?
Yes
No
7.3
Use cleanup method specified for the determinative method
7.5
Concentrate sample to required volume
Stop

METHOD 3610

ALUMINA COLUMN CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Scope: Alumina is a highly porous and granular form of aluminum oxide. It is available in three pH ranges (basic, neutral, and acidic) for use in column chromatography. It is used to separate analytes from interfering compounds of a different chemical polarity.

1.2 General Applications (Gordon and Ford):

1.2.1 **Basic** (B) pH (9-10): USES: Basic and neutral compounds stable to alkali, alcohols, hydrocarbons, steroids, alkaloids, natural pigments. DISADVANTAGES: Can cause polymerization, condensation, and dehydration reactions; cannot use acetone or ethyl acetate as eluants.

1.2.2 **Neutral** (N): USES: Aldehydes, ketones, quinones, esters, lactones, glycoside. DISADVANTAGES: Considerably less active than the basic form.

1.2.3 **Acidic** (A) pH (4-5): USES: Acidic pigments (natural and synthetic), strong acids (that otherwise chemisorb to neutral and basic alumina).

1.2.4 **Activity grades**: Acidic, basic, or neutral alumina can be prepared in various activity grades (I to V), according to the Brockmann scale, by addition of H_2O to Grade 1 (prepared by heating at 400-450°C until no more H_2O is lost). The Brockmann scale (Gordon and Ford, p. 374) is reproduced below:

Water added (wt. %):	0	3	6	10	15
Activity grade:	I	II	III	IV	V
RF (p-aminoazobenzene):	0.0	0.13	0.25	0.45	0.55

1.3 Specific applications: This method includes guidance for cleanup of sample extracts containing phthalate esters and nitrosamines. For alumina column cleanup of petroleum wastes, see Method 3611.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution of the analytes is effected with a suitable solvent(s), leaving the interfering compounds on the column. The eluate is then concentrated.

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Chromatography column: 300-mm x 10-mm I.D., with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Beakers: 500-mL.

4.3 Reagent bottle: 500-mL.

4.4 Muffle furnace.

4.5 Kuderna-Danish (K-D) apparatus:

4.5.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.5.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.5.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.5.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.6 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.7 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.8 Vials: Glass, 2-mL capacity, with Teflon-lined screw cap.

4.9 Erlenmeyer flasks: 50- and 250-mL.

5.0 REAGENTS

5.1 Sodium sulfate: (ACS) Granular, anhydrous (purified by heating at 400°C for 4 hr in a shallow tray).

5.2 Eluting solvents:

5.2.1 **Diethyl ether:** Pesticide quality or equivalent.

5.2.1.1 Must be free of peroxides, as indicated by EM Quant test strips (test strips are available from EM Laboratories Inc., 500 Executive Blvd., Elmsford, New York 10523).

5.2.1.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL ethyl alcohol preservative must be added to each liter of ether.

5.2.2 **Methanol, pentane, hexane, methylene chloride:** Pesticide quality or equivalent.

5.3 Alumina:

5.3.1 **For cleanup of phthalate extracts:** Alumina-Neutral, activity Super I, W200 series (ICN Life Sciences Group, No. 404583). To prepare for use, place 100 g of alumina into a 500-mL beaker and heat for approximately 16 hr at 400°C. After heating, transfer to a 500-mL reagent bottle. Tightly seal and cool to room temperature. When cool, add 3 mL of reagent water. Mix thoroughly by shaking or rolling for 10 min and let it stand for at least 2 hr. Keep the bottle sealed tightly.

5.3.2 **For cleanup of nitrosamine extracts:** Alumina-Basic, activity Super I, W200 series (ICN Life Sciences Group, No. 404571, or equivalent). To prepare for use, place 100 g of alumina into a 500-mL reagent bottle and add 2 mL of reagent water. Mix the alumina preparation thoroughly by shaking or rolling for 10 min and let it stand for at least 2 hr. The preparation should be homogeneous before use. Keep the bottle sealed tightly to ensure proper activity.

5.4 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Phthalate esters:

7.1.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.1.2 Place 10 g of alumina into a chromatographic column to settle alumina and add 1 cm of anhydrous sodium sulfate to the top.

7.1.3 Pre-elute the column with 40 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 35 mL of hexane and continue the elution of the column. Discard this hexane eluate.

7.1.4 Next, elute the column with 140 mL of 20% ethyl ether in hexane (v/v) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction. No solvent exchange is necessary. Adjust the volume of the cleaned up extract to whatever volume is required (10.0 mL for Method 8060) and analyze. Compounds that elute in this fraction are as follows:

Bis(2-ethylhexyl) phthalate
Butyl benzyl phthalate
Di-n-butyl phthalate
Diethyl phthalate
Dimethyl phthalate
Di-n-octyl phthalate.

7.2 Nitrosamines:

7.2.1 Reduce the sample extract to 2 mL prior to cleanup.

7.2.2 Diphenylamine, if present in the original sample extract, must be separated from the nitrosamines if N-nitrosodiphenylamine is to be determined by this method.

7.2.3 Place 12 g of the alumina preparation into a 10-mm I.D. chromatographic column. Tap the column to settle the alumina and add 1-2 cm of anhydrous sodium sulfate to the top.

7.2.4 Pre-elute the column with 10 mL of ethyl ether/pentane (3:7)(v/v). Discard the eluate (about 2 mL) and just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract onto the column using an additional 2 mL of pentane to complete the transfer.

7.2.5 Just prior to exposure of the sodium sulfate layer to the air, add 70 mL of ethyl ether/pentane (3:7)(v/v). Discard the first 10 mL of eluate. Collect the remainder of the eluate in a 500-mL K-D flask equipped with a 10-mL concentrator tube. This fraction contains N-nitroso-di-n-propylamine.

7.2.6 Next, elute the column with 60 mL of ethyl ether/pentane (1:1)(v/v), collecting the eluate in a second 500-mL K-D flask equipped with a 10-mL concentrator tube. Add 15 mL of methanol to the K-D flask. This fraction will contain N-nitrosodimethylamine, most of the N-nitroso-di-n-propylamine, and any diphenylamine that is present.

7.2.7 Concentrate both fractions, but use pentane to prewet the Snyder column. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of pentane. Adjust the final volume to whatever is required in the appropriate determinative method (Section 4.3 of this chapter). Analyze the fractions.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.2 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

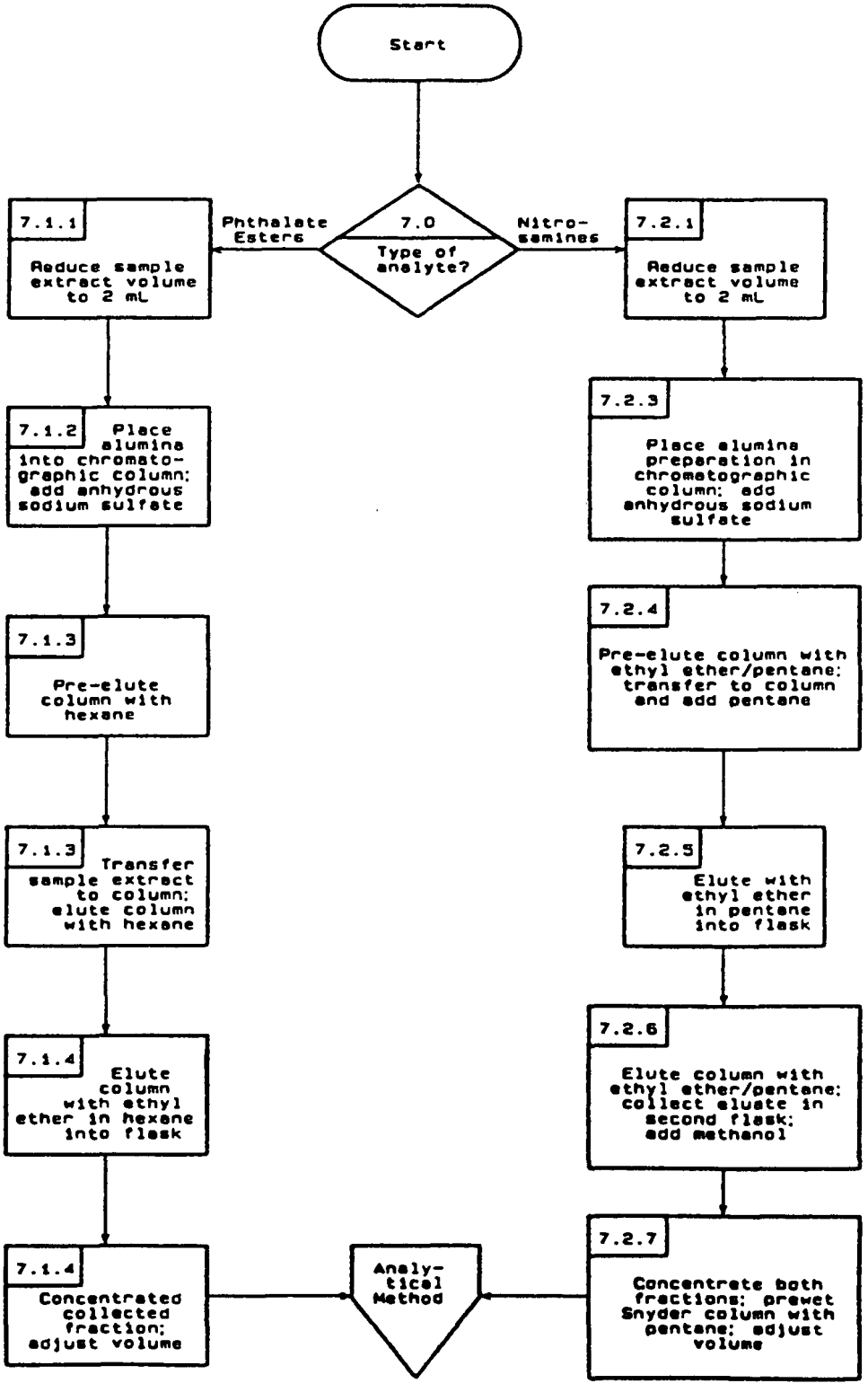
10.0 REFERENCES

1. Gordon, A.J. and R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References (New York: John Wiley & Sons, Inc.), pp. 372, 374, and 375, 1972.

2. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

METHOD 3610

ALUMINA COLUMN CLEANUP



Revision 0
Date September 1986

METHOD 3611

ALUMINA COLUMN CLEANUP AND SEPARATION OF PETROLEUM WASTES

1.0 SCOPE AND APPLICATION

1.1 Method 3611 was formerly Method 3570 in the Second Edition of this manual.

1.2 Scope: Alumina is a highly porous and granular form of aluminum oxide. It is available in three pH ranges (basic, neutral, and acidic) for use in column chromatography. It is used to separate analytes from interfering compounds of a different chemical polarity.

1.2 General Applications (Gordon and Ford):

1.2.1 **Basic** (B) pH (9-10): USES: Basic and neutral compounds stable to alkali, alcohols, hydrocarbons, steroids, alkaloids, natural pigments. DISADVANTAGES: Can cause polymerization, condensation, and dehydration reactions; cannot use acetone or ethyl acetate as eluants.

1.2.2 **Neutral** (N): USES: Aldehydes, ketones, quinones, esters, lactones, glycoside. DISADVANTAGES: Considerably less active than the basic form.

1.2.3 **Acidic** (A) pH (4-5): USES: Acidic pigments (natural and synthetic), strong acids (that otherwise chemisorb to neutral and basic alumina).

1.2.4 **Activity grades**: Acidic, basic, or neutral alumina can be prepared in various activity grades (I to V), according to the Brockmann scale, by addition of H_2O to Grade 1 (prepared by heating at 400-450°C until no more H_2O is lost). The Brockmann scale (Gordon and Ford, p. 374) is reproduced below:

Water added (wt. %):	0	3	6	10	15
Activity grade:	I	II	III	IV	V
RF (p-aminoazobenzene):	0.0	0.13	0.25	0.45	0.55

1.3 Specific applications: This method includes guidance for separation of petroleum wastes into aliphatic, aromatic, and polar fractions.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution of the analytes is effected with a suitable solvent(s), leaving the interfering compounds on the column. The eluate is then concentrated.

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.3 Caution must be taken to prevent overloading of the chromatographic column. As the column loading for any of these types of wastes approaches 300 mg of extractable organics, separation recoveries will suffer. If overloading is suspected, an aliquot of the base-neutral extract prior to cleanup may be weighed and then evaporated to dryness. A gravimetric determination on the aliquot will indicate the weight of extractable organics in the sample.

4.0 APPARATUS AND MATERIALS

4.1 Chromatography column: 300-mm x 10-mm I.D., with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Beakers: 500-mL.

4.3 Reagent bottle: 500-mL.

4.4 Muffle furnace.

4.5 Kuderna-Danish (K-D) apparatus:

4.5.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.5.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.5.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.5.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.6 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.7 Water bath: Heated with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.8 Erlenmeyer flasks: 50- and 250-mL.

5.0 REAGENTS

5.1 Sodium sulfate: (ACS) Granular, anhydrous (purified by heating at 400°C for 4 hr in a shallow tray).

5.2 Eluting solvents: Methanol, hexane, methylene chloride (pesticide quality or equivalent).

5.3 Alumina: Neutral 80-325 MCB chromatographic grade or equivalent. Dry alumina overnight at 130°C prior to use.

5.4 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 It is suggested that Method 3650, Acid-Base Partition Cleanup, be performed on the sample extract prior to alumina cleanup.

7.2 Fill the glass chromatographic column to about 20 cm with hexane. Weigh out 10.0 g of alumina and add the alumina to the column. Gently tap the column to distribute the alumina evenly (minimize chromatographic voids). Alternatively, a slurry of alumina in hexane may be used to pack the column.

7.3 Allow the alumina to settle and then add 1.0 g of anhydrous sodium sulfate on top of the alumina.

7.4 Elute the column with 50 mL of hexane. Let the solvent flow through the column until the head of the liquid in the column is just above the sodium sulfate layer. Close the stopcock to stop solvent flow.

7.5 Transfer 1.0 mL of sample extract onto the column. Rinse out extract vial with 1 mL hexane and add it to the column immediately. To avoid overloading the column, it is suggested that no more than 300 mg of extractable organics be placed on the column (see Paragraph 3.3).

7.6 Just prior to exposure of the sodium sulfate to the air, elute the column with a total of 15 mL of hexane. If the extract is in 1 mL of hexane, and if 1 mL of hexane was used as a rinse, then 13 mL of additional hexane should be used. Collect the effluent in a 50-mL flask and label this fraction "base/neutral aliphatics." Adjust the flow rate to 2 mL/min.

7.7 Elute the column with 100 mL of methylene chloride and collect the effluent in a 250-mL flask. Label this fraction "base/neutral aromatics."

7.8 Elute the column with 100 mL of methanol and collect the effluent in a 250-mL flask. Label this fraction "base/neutral polars."

7.9 Concentrate the extracts by the standard K-D technique to whatever volume is required (1-10 mL) in the appropriate determinative method (Section 4.3 of this chapter). Analyze whichever fractions contain the analytes of interest.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

9.2 A rag oil sample was analyzed by a number of laboratories according to the procedure outlined in this method. The results of these analyses for selected components in the rag oil are presented in Table 1. Reconstructed ion chromatograms from the GC/MS analyses are included as Figures 1 and 2.

10.0 REFERENCES

1. Gordon, A.J. and R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References (New York: John Wiley & Sons, Inc.), pp. 372, 374, and 375, 1972.

2. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

Table 1. RESULTS OF ANALYSIS FOR SELECTED COMPONENTS IN RAG OIL

Compound	Mean Conc. (ug/g)[a]	Standard Deviation	%RSD[b]
Naphthalene	216	42	19
Fluorene	140	66	47
Phenanthrene	614	296	18
2-Methylnaphthalene	673	120	18
Dibenzothiophene	1084	286	26
Methylphenanthrene	2908	2014	69
Methyldibenzothiophene	2200	1017	46
	Average Surrogate Recoveries		
Nitrobenzene-d_5	58.6	11	
Terphenyl-d_{14}	83.0	2.6	
Phenol-d_6	80.5	27.6	
Naphthalene-d_8	64.5	5.0	

[a] Based on five determinations from three laboratories.

[b] Percent Relative Standard Deviation.

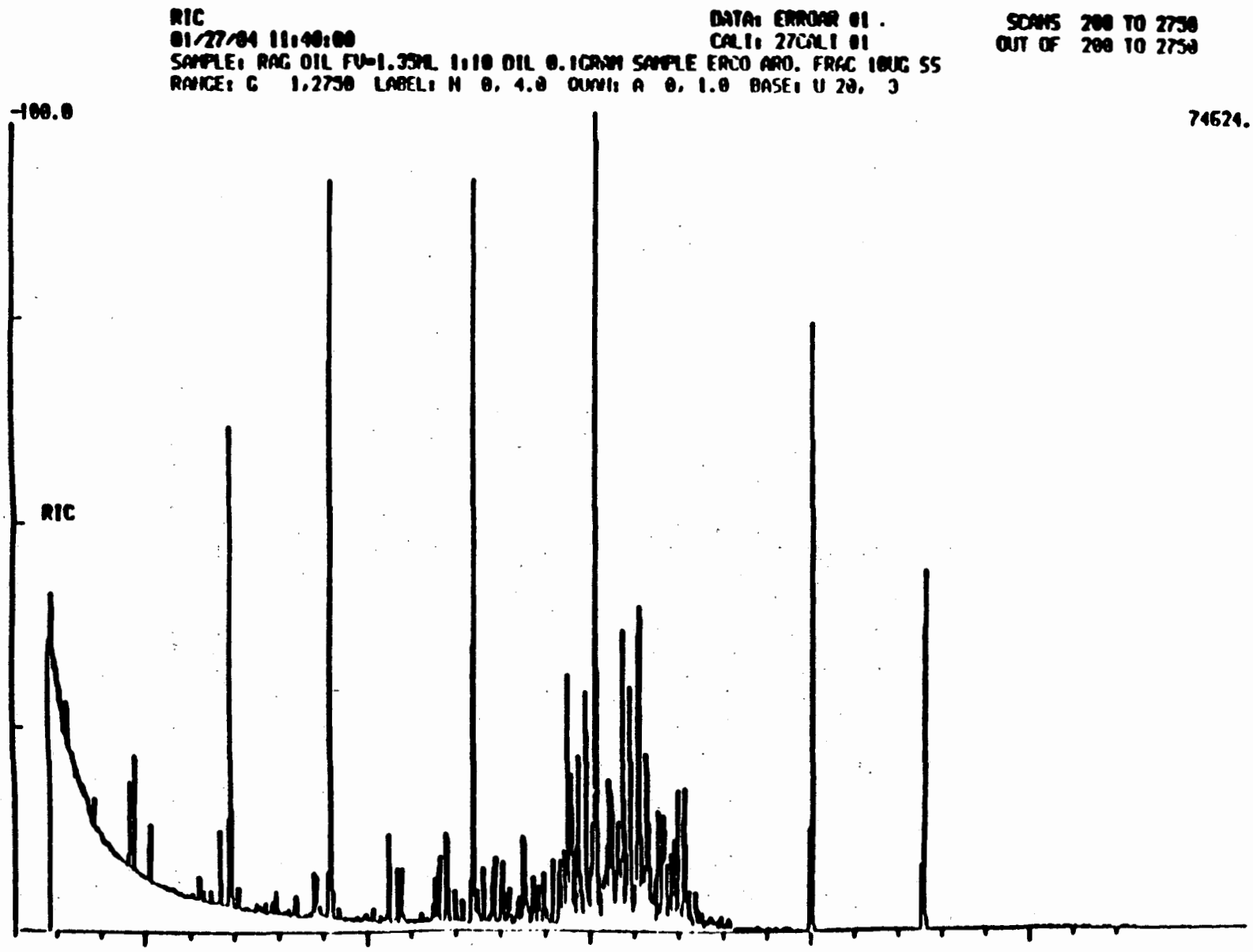


Figure 1. Reconstructed ion chromatogram from GC/MS analysis of the aromatic fraction from Rag Oil

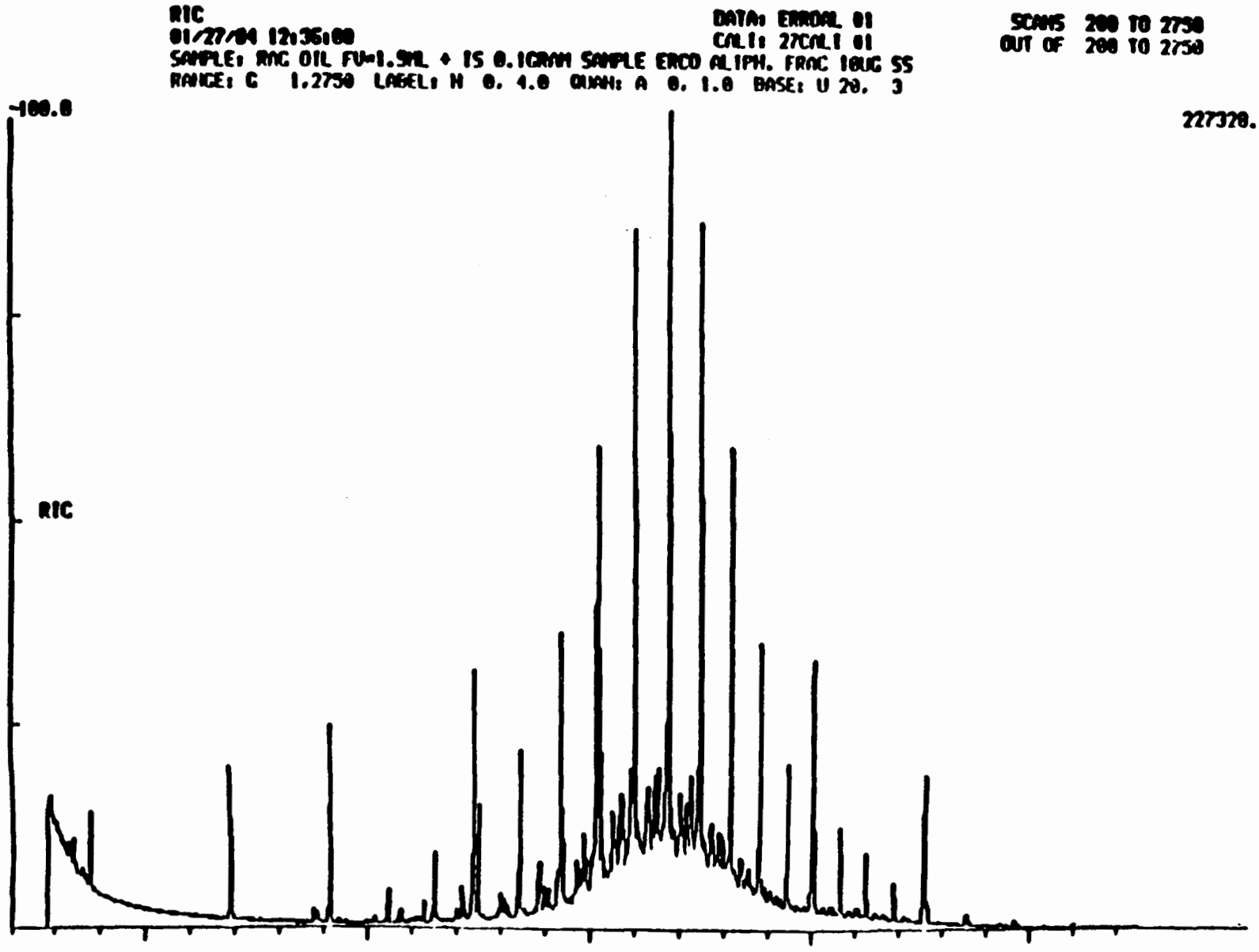
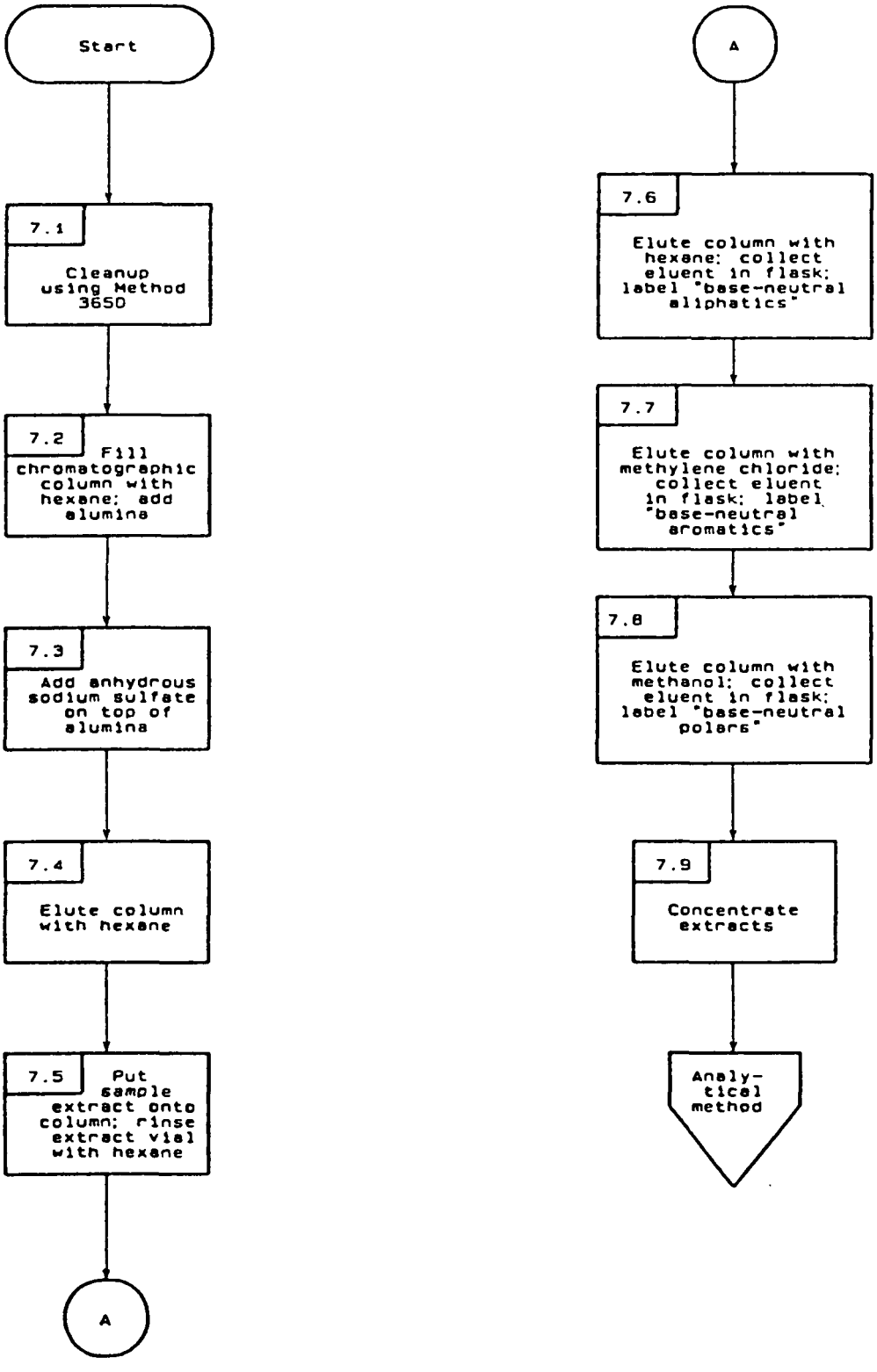


Figure 2. Reconstructed ion chromatogram from GC/MS analysis of the aliphatic fraction from Rag Oil

METHOD 3611

ALUMINA COLUMN CLEANUP AND SEPARATION OF PETROLEUM WASTES



Revision 0
Date September 1986

METHOD 3620

FLORISIL COLUMN CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Florisil, a registered tradename of the Floridin Co., is a magnesium silicate with acidic properties. It is used for general column chromatography as a cleanup procedure prior to sample analysis by gas chromatography.

1.2 General applications: Cleanup of pesticide residues and other chlorinated hydrocarbons; the separation of nitrogen compounds from hydrocarbons; the separation of aromatic compounds from aliphatic-aromatic mixtures; and similar applications for use with fats, oils, and waxes (Floridin). Additionally, Florisil is considered good for separations with steroids, esters, ketones, glycerides, alkaloids, and some carbohydrates (Gordon and Ford).

1.3 Specific applications: This method includes guidance for cleanup of sample extracts containing the following analyte groups: phthalate esters; nitrosamines; organochlorine pesticides; nitroaromatics; haloethers; chlorinated hydrocarbons; and organophosphorous pesticides.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution is effected with a suitable solvent(s) leaving the interfering compounds on the column. The eluate is then concentrated.

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Beaker: 500-mL.

4.2 Chromatographic column: 300-mm long x 10-mm I.D. or 400-mm long x 20-mm I.D., to be specified in Paragraph 7.0; with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits

may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 **Evaporation flask:** 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

4.3.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4 Muffle furnace.

4.5 Reagent bottle: 500-mL.

4.6 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.7 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.8 Erlenmeyer flasks: 50- and 250-mL.

5.0 REAGENTS

5.1 Florisil: Pesticide residue (PR) grade (60/100 mesh); purchase-activated at 1250°F (677°C), stored in glass containers with ground-glass stoppers or foil-lined screw caps.

5.1.1 **Deactivation of Florisil:** for cleanup of phthalate esters. To prepare for use, place 100 g of Florisil into a 500-mL beaker and heat for approximately 16 hr at 40°C. After heating, transfer to a 500-mL reagent bottle. Tightly seal and cool to room temperature. When cool add 3 mL of reagent water. Mix thoroughly by shaking or rolling for 10 min and let stand for at least 2 hr. Keep the bottle sealed tightly.

5.1.2 **Activation of Florisil:** for cleanup of nitrosamines, organochlorine pesticides and PCBs, nitroaromatics, haloethers, chlorinated hydrocarbons, and organophosphorous pesticides. Just before use, activate each batch at least 16 hr at 130°C in a glass container loosely covered with aluminum foil. Alternatively, store the Florisil in an oven at 130°C. Cool the Florisil before use in a desiccator.

(Florisil from different batches or sources may vary in adsorptive capacity. To standardize the amount of Florisil which is used, the use of lauric acid value is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per g of Florisil. The amount of Florisil to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 g (Mills).)

5.2 Sodium sulfate (ACS): Granular, anhydrous (purified by heating at 400°C for 4 hr in a shallow tray).

5.3 Eluting solvents:

5.3.1 **Diethyl ether:** Pesticide quality or equivalent.

5.3.1.1 Must be free of peroxides as indicated by EM Quant test strips (available from EM Laboratories Inc., 500 Executive Boulevard, Elmsford, NY 10523).

5.3.1.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL ethyl alcohol preservative must be added to each liter of ether.

5.3.2 **Acetone; hexane; methylene chloride; pentane; petroleum ether** (boiling range 30-60°C): Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Phthalate esters:

7.1.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.1.2 Place 10 g of Florisil into a 10-mm I.D. chromatographic column. Tap the column to settle the Florisil and add 1 cm of anhydrous sodium sulfate to the top.

7.1.3 Preelute the column with 40 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 40 mL of hexane and continue the elution of the column. Discard this hexane eluate.

7.1.4 Next, elute the column with 100 mL of 20% ethyl ether in hexane (v/v) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction. No solvent exchange is necessary. Adjust the volume of the cleaned-up extract to whatever volume is required (10 mL for Method 8060) and analyze by gas chromatography. Compounds that elute in this fraction are:

Bis(2-ethylhexyl)phthalate
Butyl benzyl phthalate
Di-n-butyl phthalate
Diethyl phthalate
Dimethyl phthalate
Di-n-octyl phthalate

7.2 Nitrosamines:

7.2.1 Reduce the sample extract volume to 2 mL prior to cleanup.

7.2.2 Place 22 g of activated Florisil into a 20-mm I.D. chromatographic column. Tap the column to settle the Florisil and add about 5 mm of anhydrous sodium sulfate to the top.

7.2.3 Preelute the column with 40 mL of ethyl ether/pentane (15:85) (v/v). Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract onto the column using an additional 2 mL of pentane to complete the transfer.

7.2.4 Elute the column with 90 mL of ethyl ether/pentane (15:85) (v/v) and discard the eluate. This fraction will contain the diphenylamine, if it is present in the extract.

7.2.5 Next, elute the column with 100 mL of acetone/ethyl ether (5:95) (v/v) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. This fraction will contain all of the nitrosamines listed in the scope of the method.

7.2.6 Add 15 mL of methanol to the collected fraction, concentrate using pentane to prewet the K-D column and set the water bath at 70 to 75°C. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of pentane. Analyze by gas chromatography.

7.3 Organochlorine pesticides, haloethers, and organophosphorous pesticides (see Tables 1 and 2 for fractionation patterns of compounds tested):

7.3.1 Reduce the sample extract volume to 10 mL prior to cleanup. The extract solvent must be hexane.

7.3.2 Add a weight of Florisil (nominally 20 g), predetermined by calibration, to a 20-mm I.D. chromatographic column. Settle the Florisil by tapping the column. Add anhydrous sodium sulfate to the top of the Florisil to form a layer 1 to 2 cm deep. Add 60 mL of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate to air, stop the elution of the hexane by closing the stopcock on the chromatographic column. Discard the eluate.

7.3.3 Adjust the sample extract volume to 10 mL with hexane and transfer it from the K-D concentrator tube to the Florisil column. Rinse the tube twice with 1-2 mL hexane, adding each rinse to the column.

7.3.4 Place a 500-mL K-D flask and clean concentrator tube under the chromatographic column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 mL of 6% ethyl ether in hexane (v/v) (Fraction 1) using a drip rate of about 5 mL/min. All of the haloethers are in this fraction. Remove the K-D flask and set aside for later concentration. Elute the column again, using 200 mL of 15% ethyl ether in hexane (v/v) (Fraction 2), into a second K-D flask. Perform a third elution using 200 mL of 50% ethyl ether in hexane (v/v) (Fraction 3), and a final elution with 200 mL of 100% ethyl ether (Fraction 4), into separate K-D flasks.

7.3.5 Concentrate the eluates by standard K-D techniques using the water bath at about 85°C (75°C for Fraction 4). Adjust the final volume to whatever volume is required (1-10 mL). Analyze by gas chromatography.

7.4 Nitroaromatics and isophorone:

7.4.1 Reduce the sample extract volume to 2 mL prior to cleanup.

7.4.2 Prepare a slurry of 10 g activated Florisil in methylene chloride/hexane (1:9) (v/v) and place the Florisil into a 10-mm I.D. chromatographic column. Tap the column to settle the Florisil and add 1 cm of anhydrous sodium sulfate to the top. Adjust the elution rate to about 2 mL/min.

7.4.3 Just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 30 mL of methylene chloride/hexane (1:9) (v/v) and continue the elution of the column. Discard the eluate.

7.4.4 Next, elute the column with 30 mL of acetone/methylene chloride (1:9) (v/v) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction, while exchanging the solvent to hexane. To exchange the solvent, reduce the elution solvent to about 10 mL. Add 50 mL of hexane, a fresh boiling chip, and return the reassembled K-D apparatus to the hot water bath. Adjust the

TABLE 1

DISTRIBUTION OF CHLORINATED PESTICIDES, PCBs, AND HALOETHERS INTO FLORISIL COLUMN FRACTIONS

Parameter	Percent Recovery by Fraction[a]		
	1	2	3
Aldrin	100		
α-BHC	100		
β-BHC	97		
δ-BHC	98		
γ-BHC	100		
Chlordane	100		
4,4'-DDD	99		
4,4'-DDE	98		
4,4'-DDT	100		
Dieldrin	0	100	
Endosulfan I	37	64	
Ensosulfan II	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96	
Endrin aldehyde	0	68	26
Haloethers	R		
Heptachlor	100		
Heptachlor epoxide	100		
Toxaphene	96		
PCB-1016	97		
PCB-1221	97		
PCB-1232	95	4	
PCB-1242	97		
PCB-1248	103		
PCB-1254	90		
PCB-1260	95		

[a]Eluant composition: Fraction 1 - 6% ethyl ether in hexane
Fraction 2 - 15% ethyl ether in hexane
Fraction 3 - 50% ethyl ether in hexane

R = Recovered (no percent recovery data presented).

SOURCE: U.S. EPA and FDA data.

TABLE 2

DISTRIBUTION OF ORGANOPHOSPHOROUS PESTICIDES
INTO FLORISIL COLUMN FRACTIONS

Parameter	Percent Recovery by Fraction[a]			
	1	2	3	4
Azinophos methyl			20	80
Bolstar (Sulprofos)	ND	ND	ND	ND
Chlorpyrifos	>80			
Coumaphos	NR	NR	NR	
Demeton	100			
Diazinon		100		
Dichlorvos	NR	NR	NR	
Dimethoate	ND	ND	ND	ND
Disulfoton	25-40			
EPN		>80		
Ethoprop	V	V	V	
Fensulfothion	ND	ND	ND	ND
Fenthion	R	R		
Malathion		5	95	
Merphos	V	V	V	
Mevinphos	ND	ND	ND	ND
Monochrotophos	ND	ND	ND	ND
Naled	NR	NR	NR	
Parathion		100		
Parathion methyl		100		
Phorate	0-62			
Ronnel	>80			
Stirophos (Tetrachlorvinphos)	ND	ND	ND	ND
Sulfotepp	V	V		
TEPP	ND	ND	ND	ND
Tokuthion (Prothiofos)	>80			
Trichloronate	>80			

[a]Eluant composition: Fraction 1 - 200 mL of 6% ethyl ether in hexane
Fraction 2 - 200 mL of 15% ethyl ether in hexane
Fraction 3 - 200 mL of 50% ethyl ether in hexane
Fraction 4 - 200 mL of 100% ethyl ether

R = Recovered (no percent recovery information presented) (U.S. FDA).
NR = Not recovered (U.S. FDA).
V = Variable recovery (U.S. FDA).
ND = Not determined.

SOURCE: U.S. EPA and FDA data.

final volume of the cleaned-up extract to whatever volume is required (1-10 mL). Compounds that elute in this fraction are:

2,4-Dinitrotoluene
2,6-Dinitrotoluene
Isophorone
Nitrobenzene.

Analyze by gas chromatography.

7.5 Chlorinated hydrocarbons:

7.5.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.5.2 Place 12 g of Florisil into a 10-mm I.D. chromatographic column. Tap the column to settle the Florisil and add 1 to 2 cm of anhydrous sodium sulfate to the top.

7.5.3 Preelute the column with 100 mL of petroleum ether. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the sample extract to the column by decantation and subsequent petroleum ether washings. Discard the eluate. Just prior to exposure of the sodium sulfate layer to the air, begin eluting the column with 200 mL of petroleum ether and collect the eluate in a 500-mL K-D flask equipped with a 10-mL concentrator tube. This fraction should contain all of the chlorinated hydrocarbons:

2-Chloronaphthalene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
1,2,4-Trichlorobenzene.

7.5.4 Concentrate the fraction, using hexane to prewet the column. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with hexane. Adjust the final volume of the cleaned-up extract to whatever volume is required (1-10 mL). Analyze by gas chromatography.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples should also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Table 1 indicates the distribution of chlorinated pesticides, PCB's, and haloethers in various Florisil column fractions.

9.2 Table 2 indicates the distribution of organophosphorous pesticides in various Florisil column fractions.

10.0 REFERENCES

1. Gordon, A.J. and R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References (New York: John Wiley & Sons, Inc.), pp. 372, 374, and 375, 1972.

2. Floridin of ITT System, Florisil: Properties, Application, Bibliography, Pittsburgh, Pennsylvania, 5M381DW.

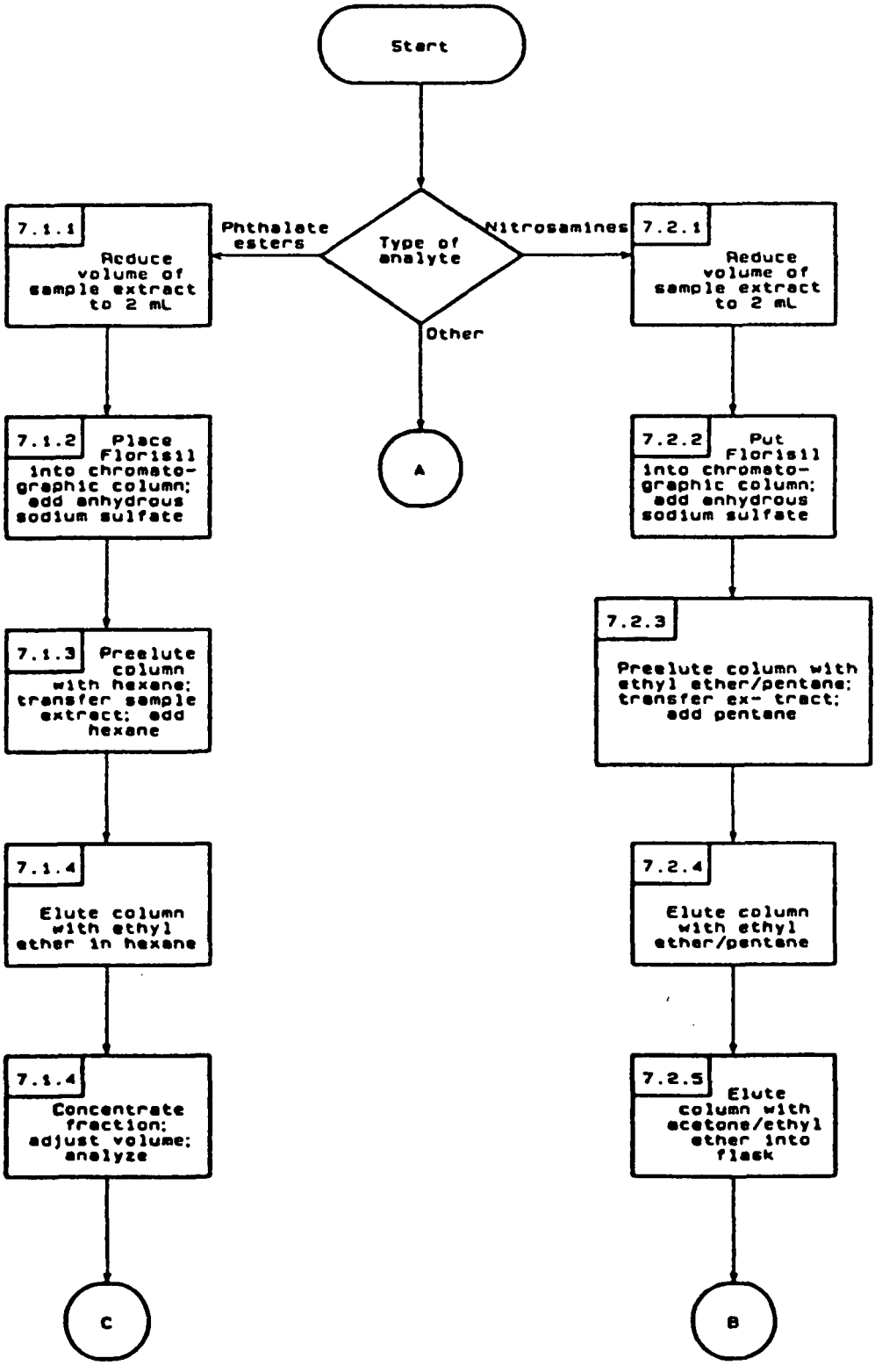
3. Mills, P.A., "Variation of Florisil Activity; Simple Method for Measuring Absorbent Capacity and its use in Standardizing Florisil Columns," Journal of the Association of Official Analytical Chemists, 51, 29, 1968.

4. U.S. Food and Drug Association, Pesticides Analytical Manual (Volume 1), July 1985.

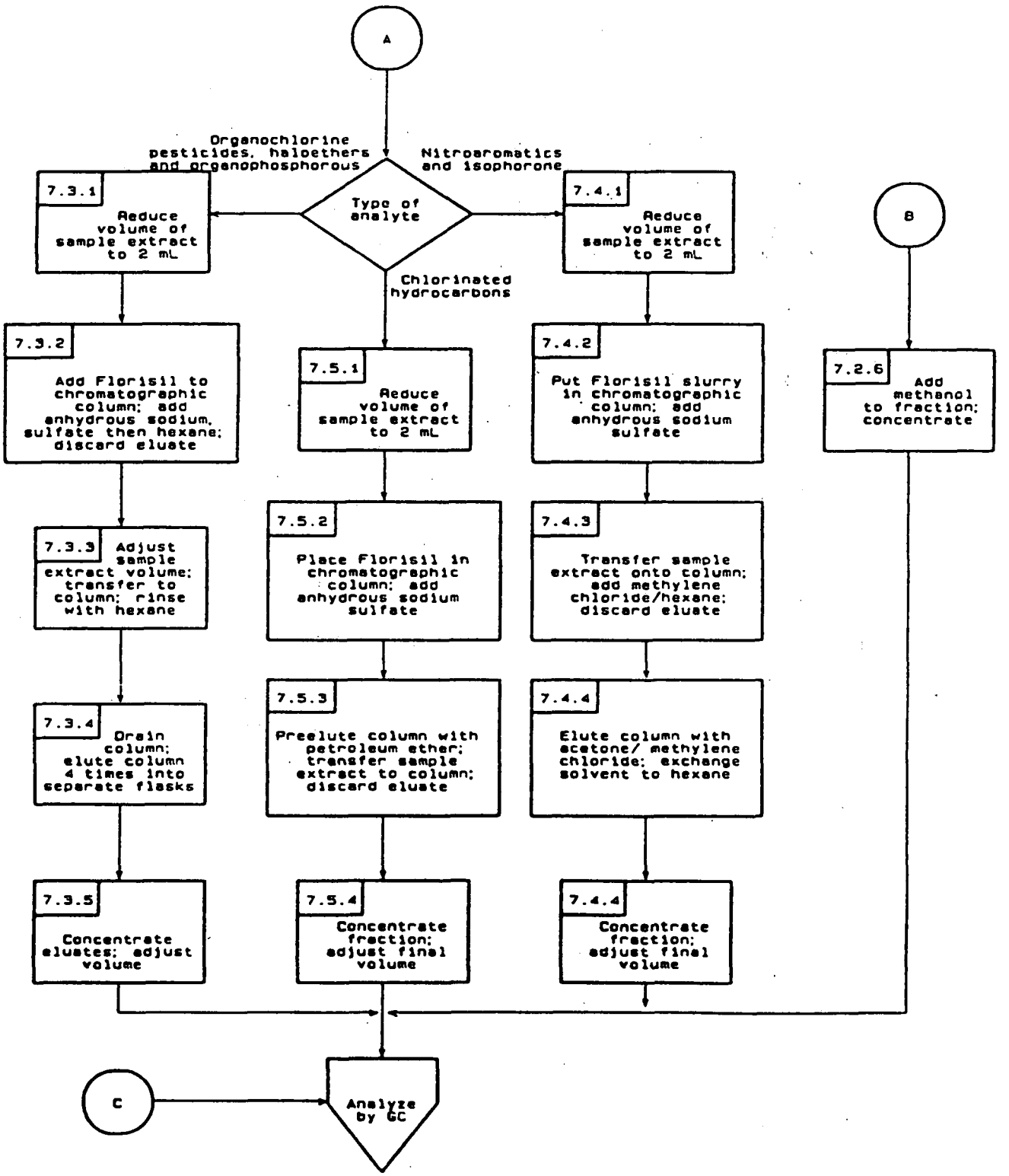
5. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

METHOD 3620

FLORISIL COLUMN CLEANUP



FLORISIL COLUMN CLEANUP
(Continued)



METHOD 3630

SILICA GEL CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Silica gel is a regenerative adsorbent of amorphous silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used for column chromatography and is for separating the analytes from interfering compounds of a different chemical polarity.

1.2 General applications (Gordon and Ford):

1.2.1 **Activated:** Heated at 150-160°C for several hours. USES: Separation of hydrocarbons.

1.2.2 **Deactivated:** Containing 10-20% water. USES: An adsorbent for most functionalities with ionic or nonionic characteristics, including alkaloids, sugar esters, glycosides, dyes, alkali metal cations, lipids, glycerides, steroids, terpenoids and plasticizers. The disadvantages of deactivated silica gel are that the solvents methanol and ethanol decrease adsorbent activity.

1.3 Specific applications: This method includes guidance for cleanup of sample extracts containing polynuclear aromatic hydrocarbons and derivatized phenolic compounds.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution of the analytes is effected with a suitable solvent(s) leaving the interfering compounds on the column. The eluate is then concentrated.

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Chromatographic column: 250-mm long x 10-mm I.D.; with Pyrex glass wool at bottom and a Teflon stopcock.
NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits

may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Beakers: 500-mL.

4.3 Kuderna-Danish (K-D) apparatus:

4.3.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 **Evaporation flask:** 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

4.3.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4 Muffle furnace.

4.5 Reagent bottle: 500-mL.

4.6 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.7 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.8 Erlenmeyer flasks: 50- and 250-mL.

5.0 REAGENTS

5.1 Silica gel: 100/200 mesh desiccant (Davison Chemical grade 923 or equivalent). Before use, activate for at least 16 hr at 130°C in a shallow glass tray, loosely covered with foil.

5.2 Sodium sulfate (ACS): Granular, anhydrous (purified by heating at 400°C for 4 hr in a shallow tray).

5.3 Eluting solvents: Cyclohexane, hexane, 2-propanol, toluene, methylene chloride, pentane (pesticide quality or equivalent).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Polynuclear aromatic hydrocarbons:

7.1.1 Before the silica gel cleanup technique can be utilized, the extract solvent must be exchanged to cyclohexane. Add 1 to 10 mL of the sample extract (in methylene chloride) and a boiling chip to a clean K-D concentrator tube. Add 4 mL of cyclohexane and attach a two-ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride to the top. Place the micro-K-D apparatus on a boiling (100°C) water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of the liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of cyclohexane. Adjust the extract volume to about 2 mL.

7.1.2 Prepare a slurry of 10 g of activated silica gel in methylene chloride and place this into a 10-mm I.D. chromatographic column. Tap the column to settle the silica gel and elute the methylene chloride. Add 1 to 2 cm of anhydrous sodium sulfate to the top of the silica gel.

7.1.3 Preelute the column with 40 mL of pentane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 2 mL cyclohexane sample extract onto the column using an additional 2 mL cyclohexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane and continue the elution of the column. Discard this pentane eluate.

7.1.4 Next, elute the column with 25 mL of methylene chloride/-pentane (2:3)(v/v) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction to whatever volume is required (1-10 mL). Proceed with HPLC or GC analysis. Components that elute in this fraction are:

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(ghi)perylene
Benzo(k)fluoranthene
Chrysene
Dibenzo(a,h)anthracene
Fluoranthene
Fluorene

Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

7.2 Derivatized phenols:

7.2.1 This silica gel cleanup procedure is performed on sample extracts that have undergone pentafluorobenzyl bromide derivatization as described in Method 8040.

7.2.2 Place 4.0 g of activated silica gel into a 10-mm I.D. chromatographic column. Tap the column to settle the silica gel and add about 2 g of anhydrous sodium sulfate to the top of the silica gel.

7.2.3 Preelute the column with 6 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, pipet onto the column 2 mL of the hexane solution that contains the derivatized sample or standard. Elute the column with 10.0 mL of hexane and discard the eluate.

7.2.4 Elute the column, in order, with: 10.0 mL of 15% toluene in hexane (Fraction 1); 10.0 mL of 40% toluene in hexane (Fraction 2); 10.0 mL of 75% toluene in hexane (Fraction 3); and 10.0 mL of 15% 2-propanol in toluene (Fraction 4). All elution mixtures are prepared on a volume:volume basis. Elution patterns for the phenolic derivatives are shown in Table 1. Fractions may be combined, as desired, depending upon the specific phenols of interest or level of interferences. Proceed with GC analysis (Method 8040).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Table 1 provides performance information on the fractionation of phenolic derivatives using this method.

10.0 REFERENCES

1. Gordon, A.J., and R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References, (New York: John Wiley & Sons, Inc.), pp. 372, 374, and 375, 1972.

2. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

TABLE 1. SILICA GEL FRACTIONATION OF PFBB DERIVATIVES

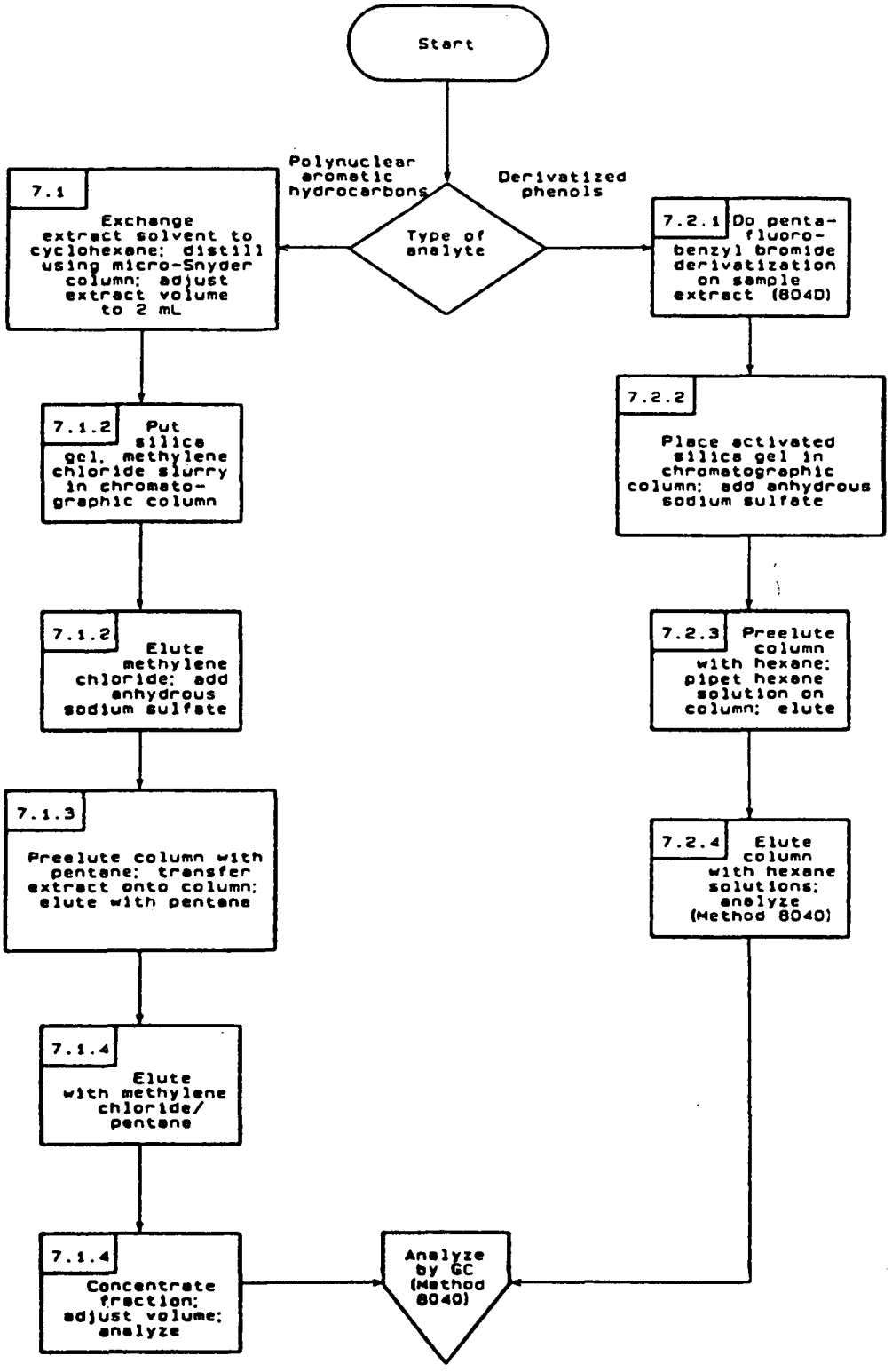
Parameter	Percent Recovery by Fraction[1]			
	1	2	3	4
2-Chlorophenol		90	1	
2-Nitrophenol			9	90
Phenol		90	10	
2,4-Dimethylphenol		95	7	
2,4-Dichlorophenol		95	1	
2,4,6-Trichlorophenol	50	50		
4-Chloro-3-methylphenol		84	14	
Pentachlorophenol	75	20		
4-Nitrophenol			1	90

[1] Eluant composition:

Fraction 1-15% toluene in hexane.
Fraction 2-40% toluene in hexane.
Fraction 3-75% toluene in hexane.
Fraction 4-15% 2-propanol in toluene.

METHOD 3630

SILICA GEL CLEANUP



METHOD 3640

GEL-PERMEATION CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Gel-permeation chromatography (GPC) is a size exclusion procedure using organic solvents and hydrophobic gels in the separation of synthetic macromolecules (Gordon and Ford). The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be greater than those of the molecules to be separated (Shugar, et al.).

1.2 General application: GPC is recommended for the elimination from the sample of lipids, polymers, copolymers, proteins, natural resins and polymers, cellular components, viruses, steroids, and dispersed high-molecular-weight compounds (Shugar, et al.).

1.3 Specific application: This method includes guidance for cleanup of sample extracts containing the compounds listed in Tables 2-1 through 2-9 of Chapter 2.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of preswelled absorbent and is flushed with solvent for an extended period. The column is calibrated and then loaded with the sample to be analyzed. Elution is effected with a suitable solvent(s) and the product is then concentrated.

3.0 INTERFERENCES

3.1 A reagent blank should be analyzed for the compound of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS

4.1 Gel permeation chromatography system: (Analytical Biochemical Laboratories, Inc. GPC autoprep Model 1002A or equivalent). An automated system of this type is not required; however, if not used, equivalency of an alternative system must be shown.

4.1.1 **Chromatographic column:** 600- to 700-mm x 25-mm I.D. glass column fitted for upward flow operation.

4.1.2 **Bio-beads S-X3:** 70 g per column.

4.1.3 **Pump:** Capable of constant flow of 0.1 to 5 mL/min at up to 100 psi.

4.1.4 **Injector:** With 5-mL loop.

4.1.5 **Ultraviolet detector:** 254-nm (optional).

4.1.6 **Strip-chart recorder:** (optional).

4.1.7 **Syringe:** 10-mL with Luerlok fitting.

4.1.8 **Syringe filter holder and filter:** BioRad "Prep Disc" sample filter # 343-0005 and 5-um size filters or equivalent.

4.2 Beakers: 400-mL.

5.0 REAGENTS

5.1 Methylene chloride: Pesticide quality or equivalent.

5.2 GPC calibration solutions:

5.2.1 **Corn oil:** 200 mg/mL in methylene chloride.

5.2.2 **Bis(2-ethylhexyl)phthalate and pentachlorophenol solution:** 4.0 mg/mL in methylene chloride.

5.2.3 Mix the corn oil with the phthalate/phenol solution if a UV detector is used. The concentrations should remain the same.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Packing the column: Place approximately 70 g of Bio Beads SX-3 in a 400-mL beaker. Cover the beads with methylene chloride; allow the beads to swell overnight (before packing the columns). Transfer the swelled beads to the column and start pumping solvent through the column, from bottom to top, at 5.0 mL/min. After approximately 1 hr, adjust the pressure on the column to 7-10 psi and pump an additional 4 hr to remove air from the column. Adjust the column pressure periodically as required to maintain 7-10 psi. (See the instrument manual for more details on packing the column.) The pressure should not be permitted to exceed 25 psi.

7.2 Calibration of the column: The column can either be calibrated manually by gravimetric/GC/FID techniques or automatically if a recording UV detector with a flow through cell is available.

7.2.1 **Manual calibration:** Load 5 mL of the corn oil solution into sample loop No. 1 and 5 mL of the phthalate-phenol solution into loop No. 2. Inject the corn oil and collect 10-mL fractions (i.e., change fractions at 2-min intervals) for 36 min. Inject the phthalate-phenol solution and collect 15 mL fractions for 60 min. Determine the corn oil elution pattern by evaporation of each fraction to dryness followed by a gravimetric determination of the residue. Analyze the phthalate-phenol fractions by GC/FID using a DB-5 capillary column, a UV spectrophotometer, or a GC/MS system. Plot the concentration of each component in each fraction versus total eluant volume (or time) from the injection points. Choose a dump time which allows $\geq$ 85% removal of the corn oil and $\geq$ 85% recovery of the bis(2-ethylhexyl)phthalate. Choose the collect time to extend at least 10 min after the elution of pentachlorophenol. Wash the column with methylene chloride at least 15 min between samples. Typical parameters selected are: Dump time, 30 min (150 mL); collect time, 36 min (180 mL); and wash time, 15 min (75 mL).

7.2.2 **Automated calibration:** The column can also be calibrated by the use of a 254-nm detector in place of gravimetric and GC analyses of fractions. Use the corn oil/phthalate/phenol mixture when using a UV detector. Load 5 mL into sample loop No. 1. Use the same criteria for choosing dump time and collect time as in the manual calibration.

7.2.3 The SX-3 Bio Beads column may be reused for several months, even if discoloration occurs. Recalibrate the system once a week.

7.3 GPC Extract Cleanup: The extract must be in methylene chloride or, primarily methylene chloride. All other solvents must be concentrated to 1 mL and diluted to 10.0 mL with methylene chloride. Prefilter or load all extracts via the filter holder to avoid particulates that might cause flow stoppage or damage the valve. Load one 5.0 mL aliquot of the extract onto the GPC column. Do not apply excessive pressure when loading. Purge the sample loading tubing thoroughly with solvent between extracts. After especially dirty extracts, run a GPC blank (methylene chloride) to check for carry-over. Process the extracts using the dump, collect, and wash parameters determined from the calibration, and collect the cleaned extracts in 400-mL beakers tightly covered with aluminum foil.

NOTE: Half of the 10.0 mL extract is lost during the loading of the GPC. Therefore, divide the sample size by two when calculating analyte concentration.

7.4 Concentrate the extract by the standard K-D technique (see any of the extraction methods, Section 4.2 of this chapter). See the determinative methods (Chapter Four, Section 4.3) for the required final volume.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedure.

8.2 The analyst should demonstrate that the compound(s) of interest are being quantitatively recovered before applying this method to actual samples.

8.2 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. Gordon, A.J., and R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References (New York: John Wiley & Sons, Inc.) pp. 372, 374, and 375, 1972.

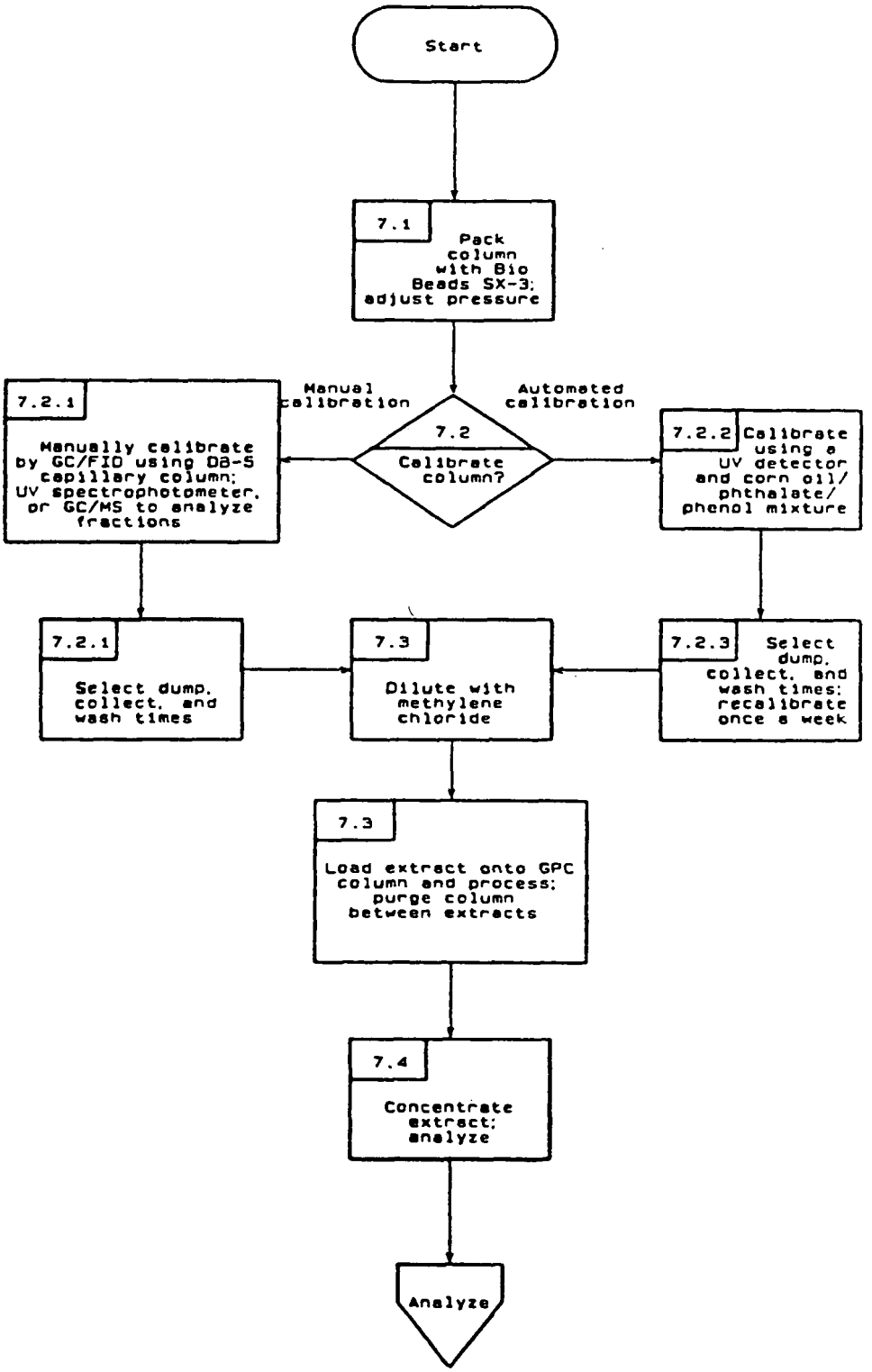
2. Shugar G.J., et al., Chemical Technician's Ready Reference Handbook, 2nd ed. (New York: McGraw-Hill Book Co.) pp. 764-766, 1981.

3. Wise, R.H., D.F. Bishop, R.T. Williams, and B.M. Austern, "Gel Permeation Chromatography in the GC/MS Analysis of Organics in Sludges," U.S. EPA, Municipal Environmental Research Laboratory, Cincinnati, Ohio 45268.

4. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, Revision, July 1985.

METHOD 3640

GEL-PERMEATION CLEANUP



Revision 0
Date September 1986

METHOD 3650

ACID-BASE PARTITION CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Method 3650 was formally Method 3530 in the second edition of this manual.

1.2 This is a liquid-liquid partitioning method to separate acid analytes from base/neutral analytes using pH adjustment. It may be used for cleanup of petroleum waste prior to alumina cleanup.

2.0 SUMMARY OF METHOD

2.1 The solvent extract is shaken with water that is strongly basic. The acid analytes partition into the aqueous layer, whereas, the basic and neutral compounds stay in the organic solvent. The base/neutral fraction is concentrated and is ready for further cleanup, if necessary, or analysis. The aqueous layer is acidified and extracted with an organic solvent. This extract is concentrated and then ready for analysis for the acid analytes.

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compound of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Separatory funnel: 125-mL, with Teflon stopcock.

4.2 Drying column: 20-mm I.D. Pyrex chromatographic column; with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus:

4.3.1 **Concentrator tube:** 10-mL, graduated (Kontes K5700-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 **Evaporation flask:** 500-mL (K-570001-0500 or equivalent). Attach to concentrator tube with springs.

4.3.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 **Snyder column:** Two-ball micro (Kontes K569001-0219 or equivalent).

4.4 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.6 Vials: Glass, 2-mL capacity with Teflon-lined screw-cap.

4.7 pH indicator paper: pH range including the desired extraction pH.

4.8 Erlenmeyer flask: 125-mL.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2 Sodium hydroxide solution 10N: (ACS) 40 g NaOH in reagent water and dilute to 100 mL.

5.3 Sodium sulfate: (ACS) Granular, anhydrous (purified by heating at 400°C for 4 hr in a shallow tray).

5.4 Sulfuric acid solution (1:1): Slowly add 50 mL H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

5.5 Solvents: Acetone, methanol, ethyl ether, methylene chloride (pesticide quality or equivalent).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Place 10 mL of the extract or organic liquid waste to be cleaned up into the separatory funnel.

7.2 Add 20 mL of methylene chloride to the separatory funnel.

7.3 Add 20 mL of reagent water and adjust the pH to 12-13 with sodium hydroxide.

7.4 Seal and shake the separatory funnel for 1-2 min with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once.

7.5 Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third of the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

7.6 Separate the aqueous phase and transfer it to a 125-mL Erlenmeyer flask. Repeat the extraction two more times using fresh 20 mL portions of reagent water pH 12-13. Combine the aqueous extracts.

7.7 At this point the analytes will be in the organic and/or in the aqueous phase. Organic acids and phenols will be in the aqueous phase, whereas, base/neutral analytes will be in the organic solvent. If the analytes are in the aqueous phase only, discard the organic phase and proceed to Paragraph 7.8. If the analytes are in the organic phase, discard the aqueous phase and proceed to Paragraph 7.10.

7.8 Transfer the aqueous phase to a clean separatory funnel. Adjust the aqueous layer to a pH of 1-2 with sulfuric acid. Add 20 mL of methylene chloride to the separatory funnel and shake for 2 min. Allow the solvent to separate from the aqueous phase and collect the solvent in an Erlenmeyer flask.

7.9 Add a second 20 mL volume of methylene chloride to the separatory funnel and re-extract at pH 1-2 a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

7.10 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.11 Dry the extracts by passing them through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in the K-D concentrator. Rinse the Erlenmeyer flask which contained the solvent extract and the column with 20 mL of methylene chloride to complete the quantitative transfer.

7.12 Add one or two boiling chips to the flask and attach a three-ball macro-Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot

water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of extraction solvent.

7.13 Add another one or two boiling chips to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride to the top of the column. Place the K-D apparatus in a hot water bath (95°-100°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of the liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain for at least 10 min while cooling. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 0.2 mL of extraction solvent. Adjust the final volume to 1.0 mL with solvent.

7.14 The acid fraction is now ready for analysis. If the base/neutral extract is to undergo further cleanup by the Alumina Column Cleanup for Petroleum Waste (Method 3611), the extract must be exchanged to hexane. To the 1-mL base/neutral extract, 5 mL of hexane should be added (solvent exchanged), and this mixture then reconcentrated to 1 mL using the micro-KD apparatus. If no further cleanup of the base/neutral extract is required, it is also ready for analysis.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples must be processed through this cleanup method.

9.0 METHOD PERFORMANCE

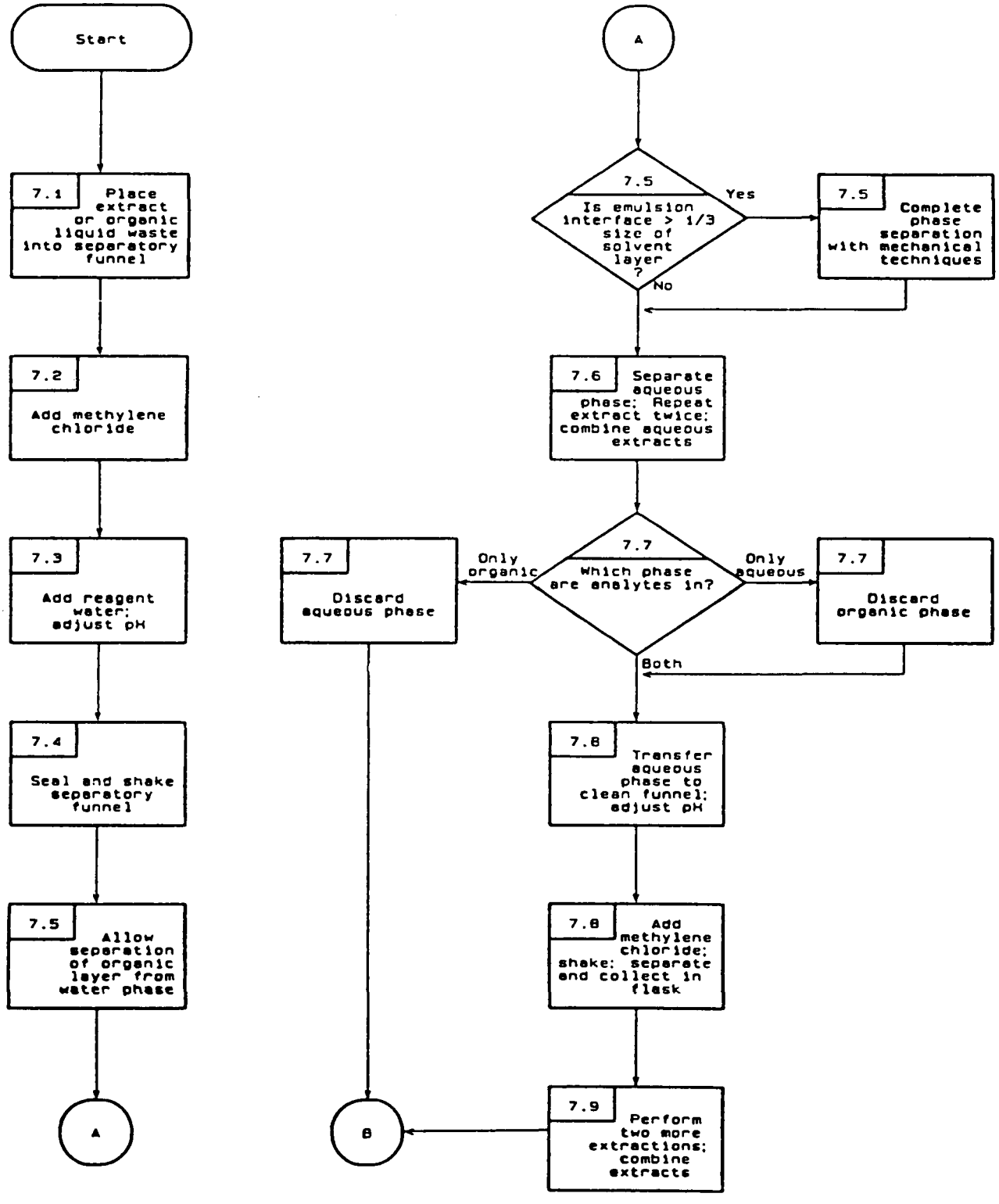
9.1 Refer to the determinative methods for performance data.

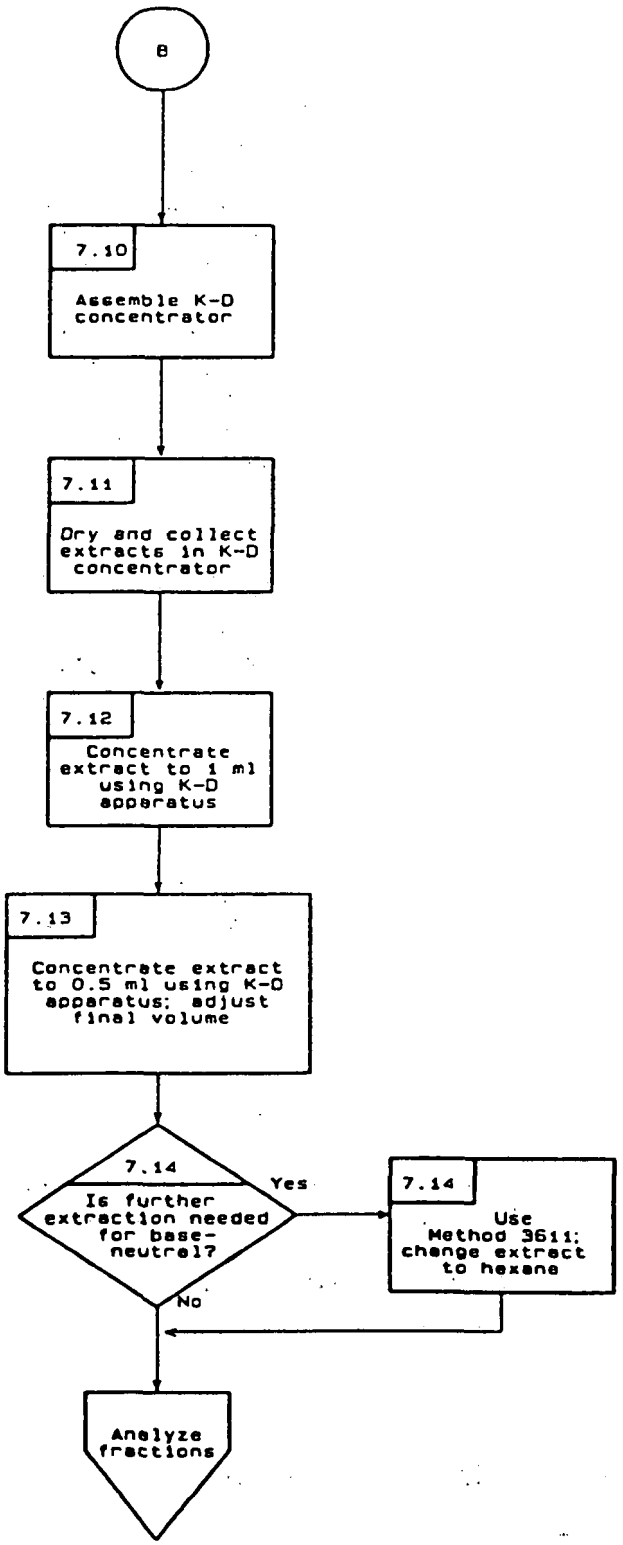
10.0 REFERENCES

10.1 None required.

METHOD 3650

ACID-BASE PARTITION CLEANUP




B
7.10
Assemble K-D concentrator
7.11
Dry and collect extracts in K-D concentrator
7.12
Concentrate extract to 1 ml using K-D apparatus
7.13
Concentrate extract to 0.5 ml using K-D apparatus; adjust final volume
7.14
Is further extraction needed for base-neutral?
Yes
No
7.14
Use Method 3611; change extract to hexane
Analyze fractions

METHOD 3660

SULFUR CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Elemental sulfur is encountered in many sediment samples (generally specific to different areas in the country), marine algae, and some industrial wastes. The solubility of sulfur in various solvents is very similar to the organochlorine and organophosphorous pesticides; therefore, the sulfur interference follows along with the pesticides through the normal extraction and cleanup techniques. In general, sulfur will usually elute entirely in Fraction 1 of the Florisil cleanup (Method 3620).

1.2 Sulfur will be quite evident in gas chromatograms obtained from electron capture detectors, flame photometric detectors operated in the sulfur or phosphorous mode, and Coulson electrolytic conductivity detectors in the sulfur mode. If the gas chromatograph is operated at the normal conditions for pesticide analysis, the sulfur interference can completely mask the region from the solvent peak through Aldrin.

1.3 Three techniques for the elimination of sulfur are detailed within this method: (1) the use of copper powder; (2) the use of mercury; and (3) the use of tetrabutylammonium-sulfite. Tetrabutylammonium-sulfite causes the least amount of degradation of a broad range of pesticides and organic compounds, while copper and mercury may degrade organophosporous and some organochlorine pesticides.

2.0 SUMMARY OF METHOD

2.1 The sample to undergo cleanup is mixed with either copper, mercury, or tetrabutylammonium (TBA)-sulfite. The mixture is shaken and the extract is removed from the sulfur cleanup reagent.

3.0 INTERFERENCES

3.1 Removal of sulfur using copper:

3.1.1 The copper must be very reactive; therefore, all oxides of copper must be removed so that the copper has a shiny, bright appearance.

3.1.2 The sample extract must be vigorously agitated with the reactive copper for at least one minute.

4.0 APPARATUS AND MATERIALS

4.1 Mechanical shaker or mixer: Such as the Vortex Genie.

4.2 Pipets: Disposable, Pasteur type.

4.3 Centrifuge tubes: Calibrated, 12-mL.

4.4 Glass bottles or vials: 10-mL and 50-mL, with Teflon-lined screw-caps.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2 Nitric acid: Dilute.

5.3 Acetone, hexane, 2-propanol: Pesticide quality or equivalent.

5.4 Copper powder: Remove oxides by treating with dilute nitric acid, rinse with distilled water to remove all traces of acid, rinse with acetone and dry under a stream of nitrogen. (Copper, fine granular Mallinckrodt 4649 or equivalent).

5.5 Mercury: Triple distilled.

5.6 Tetrabutylammonium (TBA)-sulfite reagent: Dissolve 3.39 g tetrabutylammonium hydrogen sulfate in 100 mL reagent water. To remove impurities, extract this solution three times with 20-mL portions of hexane. Discard the hexane extracts, and add 25 g sodium sulfite to the water solution. Store the resulting solution, which is saturated with sodium sulfite, in an amber bottle with a Teflon-lined screw-cap. This solution can be stored at room temperature for at least one month.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Removal of sulfur using copper:

7.1.1 Concentrate the sample to exactly 1.0-mL in the Kuderna-Danish tube.

7.1.2 If the sulfur concentration is such that crystallization occurs, centrifuge to settle the crystals, and carefully draw off the sample extract with a disposable pipet leaving the excess sulfur in the K-D tube. Transfer the extract to a calibrated centrifuge tube.

7.1.3 Add approximately 2 g of cleaned copper powder (to the 0.5 mL mark) to the centrifuge tube. Mix for at least 1 min on the mechanical shaker.

7.1.4 Separate the extract from the copper by drawing off the extract with a disposable pipet and transfer to a clean vial. The volume remaining still represents 1.0 mL of extract.

NOTE: This separation is necessary to prevent further degradation of the pesticides.

7.2 Removal of sulfur using mercury:

NOTE: Mercury is a highly toxic metal and therefore, must be used with great care. Prior to using mercury, it is recommended that the analyst become acquainted with proper handling and cleanup techniques associated with this metal.

7.2.1 Concentrate the sample extract to exactly 1.0 mL.

7.2.2 Pipet 1.0 mL of the extract into a clean concentrator tube or Teflon-sealed vial.

7.2.3 Add one to three drops of mercury to the vial and seal. Agitate the contents of the vial for 15-30 sec. Prolonged shaking (2 hr) may be required. If so, use a mechanical shaker.

7.2.4 Separate the sample from the mercury by drawing off the extract with a disposable pipet and transfer to a clean vial.

7.3 Removal of sulfur using TBA-sulfite:

7.3.1 Concentrate the sample extract to exactly 1.0 mL.

7.3.2 Transfer the 1.0 mL to a 50-mL clear glass bottle or vial with a Teflon-lined screw-cap. Rinse the concentrator tube with 1 mL of hexane, adding the rinsings to the 50-mL bottle.

7.3.3 Add 1.0 mL TBA-sulfite reagent and 2 mL 2-propanol, cap the bottle, and shake for at least 1 min. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100-mg portions until a solid residue remains after repeated shaking.

7.3.4 Add 5 mL distilled water and shake for at least 1 min. Allow the sample to stand for 5-10 min. Transfer the hexane layer (top) to a concentrator tube and use the K-D technique to concentrate the extract to 1.0 mL.

7.4 Analyze the cleaned up extracts by gas chromatography (see the determinative methods, Section 4.3 of this chapter).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 All reagents should be checked prior to use to verify that interferences do not exist.

9.0 METHOD PERFORMANCE

9.1 Table 1 indicates the effect of using copper and mercury to remove sulfur on the recovery of certain pesticides.

10.0 REFERENCES

1. Loy, E.W., private communication.

2. Goerlitz, D.F. and L.M. Law, Bulletin for Environmental Contamination and Toxicology, 6, 9 (1971).

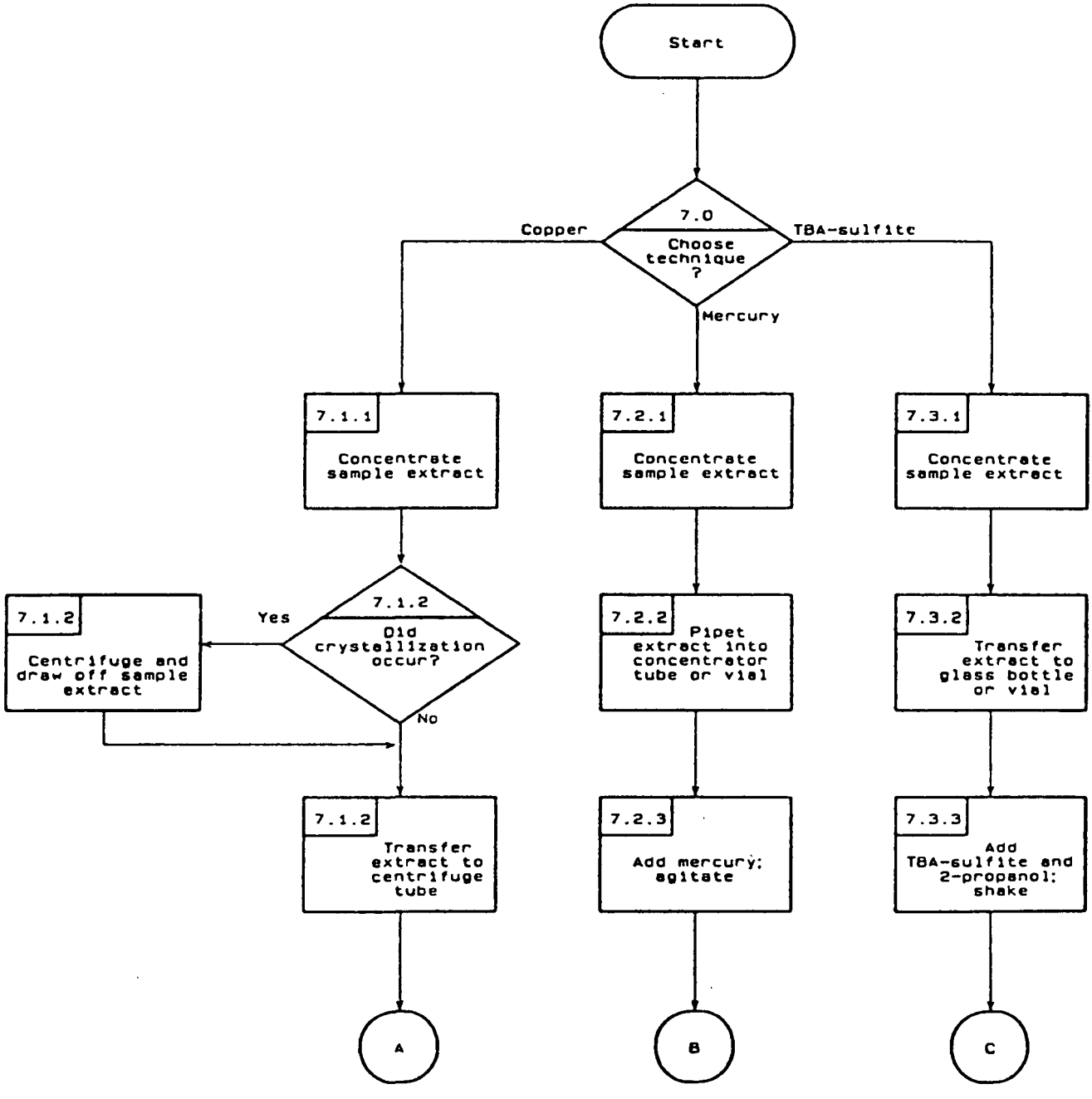
3. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, Revision, July 1985.

Table 1. EFFECT OF MERCURY AND COPPER ON PESTICIDES

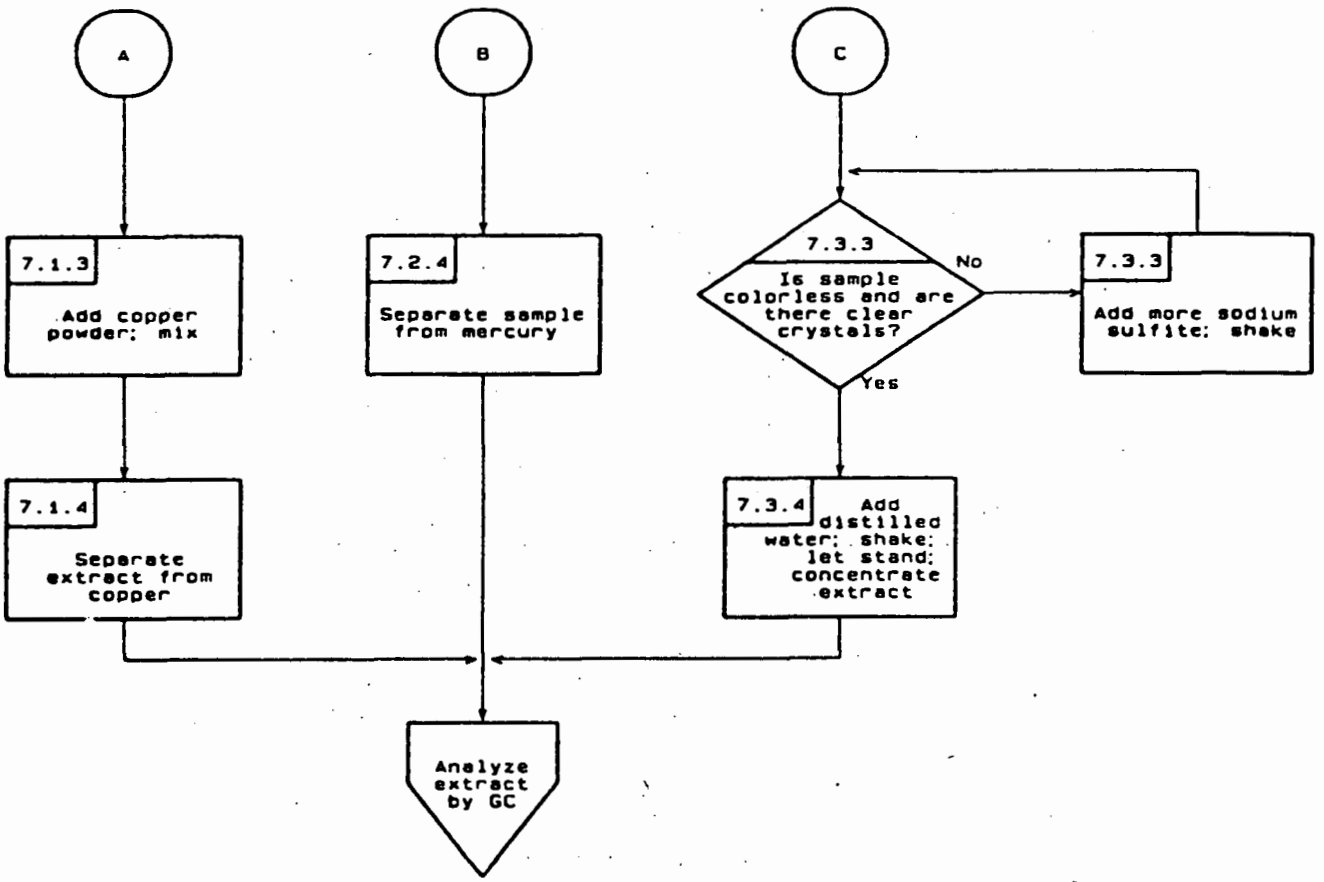
Pesticide	Percent Recovery[a] using: Mercury	Copper
Aroclor 1254	97.10	104.26
Lindane	75.73	94.83
Heptachlor	39.84	5.39
Aldrin	95.52	93.29
Heptachlor epoxide	69.13	96.55
DDE	92.07	102.91
DDT	78.78	85.10
BHC	81.22	98.08
Dieldrin	79.11	94.90
Endrin	70.83	89.26
Chlorobenzilate	7.14	0.00
Malathion	0.00	0.00
Diazinon	0.00	0.00
Parathion	0.00	0.00
Ethion	0.00	0.00
Trithion	0.00	0.00

[a] Percent recoveries cited are averages based on duplicate analyses for all compounds other than for Aldrin and BHC. For Aldrin, four and three determinations were averaged to obtain the result for mercury and copper, respectively. Recovery of BHC using copper is based on one analysis.

METHOD 3660
SULFUR CLEANUP



Revision 0
Date September 1986


A
B
C
7.1.3
Add copper powder; mix
7.2.4
Separate sample from mercury
7.3.3
Is sample colorless and are there clear crystals?
No
7.3.3
Add more sodium sulfite; shake
Yes
7.1.4
Separate extract from copper
7.3.4
Add distilled water; shake; let stand; concentrate extract
Analyze extract by GC

4.3 DETERMINATION OF ORGANIC ANALYTES

4.3.1 GAS CHROMATOGRAPHIC METHODS

METHOD 8000

GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Gas chromatography is a quantitative analytical technique useful for organic compounds capable of being volatilized without being decomposed or chemically rearranged. Gas chromatography (GC), also known as vapor phase chromatography (VPC), has two subcategories distinguished by: gas-solid chromatography (GSC), and gas-liquid chromatography (GLC) or gas-liquid partition chromatography (GLPC). This last group is the most commonly used, distinguished by type of column adsorbent or packing.

1.2 The gas chromatographic methods are recommended for use only by, or under the close supervision of, experienced residue analysts.

2.0 SUMMARY OF METHOD

2.1 Each organic analytical method that follows provides a recommended technique for extraction, cleanup, and occasionally, derivatization of the samples to be analyzed. Before the prepared sample is introduced into the GC, a procedure for standardization must be followed to determine the recovery and the limits of detection for the analytes of interest. Following sample introduction into the GC, analysis proceeds with a comparison of sample values with standard values. Quantitative analysis is achieved through integration of peak area or measurement of peak height.

3.0 INTERFERENCES

3.1 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe or purging device must be rinsed out between samples with reagent water or solvent. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank or of reagent water to check for cross contamination. For volatile samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high organohalide levels, it may be necessary to wash out the syringe or purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105°C oven between analyses.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak height and/or peak areas is recommended.

4.2 Gas chromatographic columns: See the specific determinative method. Other packed or capillary (open-tubular) columns may be used if the requirements of Section 8.6 are met.

5.0 REAGENTS

5.1 See the specific determinative method for the reagents needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Extraction: Adhere to those procedures specified in the referring determinative method.

7.2 Cleanup and separation: Adhere to those procedures specified in the referring determinative method.

7.3 The recommended gas chromatographic columns and operating conditions for the instrument are specified in the referring determinative method.

7.4 Calibration:

7.4.1 Establish gas chromatographic operating parameters equivalent to those indicated in Section 7.0 of the determinative method of interest. Prepare calibration standards using the procedures indicated in Section 5.0 of the determinative method of interest. Calibrate the chromatographic system using either the external standard technique (Section 7.4.2) or the internal standard technique (Section 7.4.3).

7.4.2 **External standard calibration procedure:**

7.4.2.1 For each analyte of interest, prepare calibration standards at a minimum of five concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with an appropriate solvent. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.4.2.2 Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g, 2- to 5-uL injections, purge-and-trap, etc.). Tabulate peak height or area responses against the mass injected.

The results can be used to prepare a calibration curve for each analyte. Alternatively, for samples that are introduced into the gas chromatograph using a syringe, the ratio of the response to the amount injected, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration. If the percent relative standard deviation (%RSD) of the calibration factor is less than 20% over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.

$$\text{Calibration factor} = \frac{\text{Total Area of Peak}^*}{\text{Mass injected (in nanograms)}}$$

*For multiresponse pesticides/PCBs use the total area of all peaks used for quantitation.

7.4.2.3 The working calibration curve or calibration factor must be verified on each working day by the injection of one or more calibration standards. The frequency of verification is dependent on the detector. Detectors, such as the electron capture detector, that operate in the sub-nanogram range are more susceptible to changes in detector response caused by GC column and sample effects. Therefore, more frequent verification of calibration is necessary. The flame ionization detector is much less sensitive and requires less frequent verification. If the response for any analyte varies from the predicted response by more than $\pm$15%, a new calibration curve must be prepared for that analyte.

$$\text{Percent Difference} = \frac{R_1 - R_2}{R_1} \times 100$$

where:

R_1 = Calibration Factor from first analysis.

R_2 = Calibration Factor from succeeding analyses.

7.4.3 **Internal standard calibration procedure:**

7.4.3.1 To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.4.3.2 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards and dilute to volume with an appropriate solvent.

One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.4.3.3 Inject each calibration standard using the same introduction technique that will be applied to the actual samples (e.g, 2- to 5-uL injection, purge-and-trap, etc.). Tabulate the peak height or area responses against the concentration of each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the analyte to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard, ug/L.

C_s = Concentration of the analyte to be measured, ug/L.

If the RF value over the working range is constant (<20% RSD), the RF can be assumed to be invariant, and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} versus RF.

7.4.3.4 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. The frequency of verification is dependent on the detector. Detectors, such as the electron capture detector, that operate in the sub-nanogram range are more susceptible to changes in detector response caused by GC column and sample effects. Therefore, more frequent verification of calibration is necessary. The flame ionization detector is much less sensitive and requires less frequent verification. If the response for any analyte varies from the predicted response by more than ±15%, a new calibration curve must be prepared for that compound.

7.5 Retention time windows:

7.5.1 Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of all single component standard mixtures and multiresponse products (i.e., PCBs) throughout the course of a 72-hr period. Serial injections over less than a 72-hr period result in retention time windows that are too tight.

7.5.2 Calculate the standard deviation of the three absolute retention times for each single component standard. For multiresponse products, choose one major peak from the envelope and calculate the

standard deviation of the three retention times for that peak. The peak chosen should be fairly immune to losses due to degradation and weathering in samples.

7.5.2.1 Plus or minus three times the standard deviation of the absolute retention times for each standard will be used to define the retention time window; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms. For multiresponse products (i.e., PCBs), the analyst should use the retention time window but should primarily rely on pattern recognition.

7.5.2.2 In those cases where the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

7.5.3 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.

7.6 Gas chromatographic analysis:

7.6.1 Introduction of organic compounds into the gas chromatograph varies depending on the volatility of the compound. Volatile organics are primarily introduced by purge-and-trap (Method 5030). However, there are limited applications where direct injection is acceptable. Use of Method 3810 or 3820 as a screening technique for volatile organic analysis may be valuable with some sample matrices to prevent overloading and contamination of the GC systems. Semivolatile organics are introduced by direct injection.

7.6.2 The appropriate detector(s) is given in the specific method.

7.6.3 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with multilevel calibration standards. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

7.6.4 **Direct Injection:** Inject 2-5 uL of the sample extract using the solvent flush technique. Smaller (1.0-uL) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 uL and the resulting peak size in area units or peak height.

7.6.5 If the responses exceed the linear range of the system, dilute the extract and reanalyze. It is recommended that extracts be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.6.6 If peak detection is prevented by the presence of interferences, further cleanup is required.

7.6.7 Examples of chromatograms for the compounds of interest are frequently available in the referring analytical method.

7.6.8 Calibrate the system immediately prior to conducting any analyses (see Paragraph 7.4). A midlevel standard must also be injected at intervals specified in the method and at the end of the analysis sequence. The calibration factor for each analyte to be quantitated, must not exceed a 15% difference when compared to the initial standard of the analysis sequence. When this criteria is exceeded, inspect the GC system to determine the cause and perform whatever maintenance is necessary (see Section 7.7) before recalibrating and proceeding with sample analysis. All samples that were injected after the sample exceeding the criteria must be reinjected.

7.6.9 Establish daily retention time windows for each analyte. Use the absolute retention time for each analyte from Section 7.6.8 as the midpoint of the window for that day. The daily retention time window equals the midpoint $\pm$ three times the standard deviation determined in Section 7.5.

7.6.9.1 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. Normally, confirmation is required: on a second GC column; by GC/MS if concentration permits; or by other recognized confirmation techniques. Confirmation may not be necessary if the composition of the sample matrix is well established by prior analyses.

7.6.9.2 Validation of GC system qualitative performance: Use the midlevel standards interspersed throughout the analysis sequence (Paragraph 7.6.8) to evaluate this criterion. If any of the standards fall outside their daily retention time window, the system is out of control. Determine the cause of the problem and correct it (see Section 7.7).

7.7 Suggested chromatography system maintenance: Corrective measures may require any one or more of the following remedial actions.

7.7.1 **Packed columns:** For instruments with injection port traps, replace the demister trap, clean, and deactivate the glass injection port insert or replace with a cleaned and deactivated insert. Inspect the injection end of the column and remove any foreign material (broken glass from the rim of the column or pieces of septa). Replace the glass wool with fresh deactivated glass wool. Also, it may be necessary to remove the first few millimeters of the packing material if any discoloration is noted, also swab out the inside walls of the column if any residue is noted. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body (described in Section 7.7.3) and/or repack/replace the column.

7.7.2 **Capillary columns:** Clean and deactivate the glass injection port insert or replace with a cleaned and deactivated insert. Break off the first few inches, up to one foot, of the injection port side of the column. Remove the column and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.

7.7.3 **Metal injector body:** Turn off the oven and remove the analytical column when oven has cooled. Remove the glass injection port insert (instruments with off-column injection or Grob). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

7.7.3.1 Place a beaker beneath the injector port inside the GC oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene; catching the rinsate in the beaker.

7.7.3.2 Prepare a solution of deactivating agent (Sylon-CT or equivalent) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, serially rinse the injector body with toluene, methanol,acetone, and hexane. Reassemble the injector and replace the GC column.

7.8 Calculations:

7.8.1 **External standard calibration:** The concentration of each analyte in the sample may be determined by calculating the amount of standard purged or injected, from the peak response, using the calibration curve or the calibration factor determined in Paragraph 7.4.2. The concentration of a specific analyte is calculated as follows:

Aqueous samples:

$$\text{Concentration (ug/L)} = [(A_X)(A)(V_t)(D)]/[(A_S)(V_i)(V_S)]$$

where:

A_X = Response for the analyte in the sample, units may be in area counts or peak height.

A = Amount of standard injected or purged, ng.

A_S = Response for the external standard, units same as for A_X.

V_i = Volume of extract injected, uL. For purge-and-trap analysis, V_i is not applicable and therefore = 1.

D = Dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

V_t = Volume of total extract, uL. For purge-and-trap analysis, V_t is not applicable and therefore = 1.

V_s = Volume of sample extracted or purged, mL.

Nonaqueous samples:

$$\text{Concentration (ng/g)} = [(A_x)(A)(V_t)(D)]/[(A_s)(V_i)(W)]$$

where:

W = Weight of sample extracted or purged, g. The wet weight or dry weight may be used, depending upon the specific applications of the data.

A_x, A_s, A, V_t, D, and V_i have the same definition as for aqueous samples.

7.8.2 **Internal standard calibration:** For each analyte of interest, the concentration of that analyte in the sample is calculated as follows:

Aqueous samples:

$$\text{Concentration (ug/L)} = [(A_x)(C_{is})(D)]/[(A_{is})(RF)(V_s)]$$

where:

A_x = Response of the analyte being measured, units may be in area counts or peak height.

C_{is} = Amount of internal standard added to extract or volume purged, ng.

D = Dilution factor, if a dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

A_{is} = Response of the internal standard, units same as A_x.

RF = Response factor for analyte, as determined in Paragraph 7.4.3.3.

V_s = Volume of water extracted or purged, mL.

Nonaqueous samples:

$$\text{Concentration (ug/kg)} = [(A_s)(C_{is})(D)]/[(A_{is})(RF)(W_s)]$$

where:

W_s = Weight of sample extracted, g. Either a dry weight or wet weight may be used, depending upon the specific application of the data.

A_s, C_{is}, D, A_{is}, and RF have the same definition as for aqueous samples.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.3 For each analytical batch (up to 20 samples), a reagent blank, matrix spike and matrix spike duplicate/duplicate must be analyzed (the frequency of the spikes may be different for different monitoring programs). The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps.

8.4 The experience of the analyst performing gas chromatography is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration sample should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g, column changed), recalibration of the system must take place.

8.5 Required instrument QC:

8.5.1 Section 7.4 requires that the %RSD vary by <20% when comparing calibration factors to determine if a five point calibration curve is linear.

8.5.2 Section 7.4 sets a limit of ±15% difference when comparing daily response of a given analyte versus the initial response. If the limit is exceeded, a new standard curve must be prepared.

8.5.3 Section 7.5 requires the establishment of retention time windows.

8.5.4 Paragraph 7.6.8 sets a limit of ±15% difference when comparing the initial response of a given analyte versus any succeeding standards analyzed during an analysis sequence.

8.5.5 Paragraph 7.6.9.2 requires that all succeeding standards in an analysis sequence must fall within the daily retention time window established by the first standard of the sequence.

8.6 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.6.1 A quality (QC) check sample concentrate is required containing each analyte of interest. The QC check sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC check sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.6.1.1 The concentration of the QC check sample concentrate is highly dependent upon the analytes being investigated. Therefore, refer to Method 3500, Section 8.0 for the required concentration of the QC check sample concentrate.

8.6.2 **Preparation of QC check samples:**

8.6.2.1 Volatile organic analytes (Methods 8010, 8020, and 8030): The QC check sample is prepared by adding 200 uL of the QC check sample concentrate (Section 8.6.1) to 100 mL of reagent water.

8.6.2.2 Semivolatile organic analytes (Methods 8040, 8060, 8080, 8090, 8100, and 8120): The QC check sample is prepared by adding 1.0 mL of the QC check sample concentrate (8.6.1) to each of four 1-L aliquots of reagent water.

8.6.3 Four aliquots of the well-mixed QC check sample are analyzed by the same procedures used to analyze actual samples (Section 7.0 of each of the methods). For volatile organics, the preparation/analysis process is purge-and-trap/gas chromatography. For semivolatile organics, the QC check samples must undergo solvent extraction (see Method 3500) prior to chromatographic analysis.

8.6.4 Calculate the average recovery ($\bar{X}$) in ug/L, and the standard deviation of the recovery (s) in ug/L, for each analyte of interest using the four results.

8.6.5 For each analyte compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, given the QC Acceptance Criteria Table at the end of each of the determinative methods. If s and $\bar{X}$ for all analytes of interest meet the acceptance

criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in each of the QC Acceptance Criteria Tables present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined.

8.6.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.6.6.1 or 8.6.6.2.

8.6.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Section 8.6.2.

8.6.6.2 Beginning with Section 8.6.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.6.2.

8.7 The laboratory must, on an ongoing basis, spike at least one sample per analytical batch (maximum of 20 samples per batch) to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.7.1 The concentration of the spike in the sample should be determined as follows:

8.7.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.7.2, whichever concentration would be larger.

8.7.1.2 If the concentration of a specific analyte in the sample is not being checked against a limit specific to that analyte, the spike should be at the same concentration as the QC check sample (8.6.2) or 1 to 5 times higher than the background concentration determined in Section 8.7.2, whichever concentration would be larger.

8.7.1.3 For semivolatile organics, it may not be possible to determine the background concentration levels prior to spiking (e.g., maximum holding times will be exceeded). If this is the case, the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or the QC check sample concentration (Section 8.6.2).

8.7.2 Analyze one unspiked and one spiked sample aliquot to determine percent recovery of each of the spiked compounds.

8.7.2.1 Volatile organics: Analyze one 5-mL sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC check sample concentrate (Section 8.6.1) appropriate for the background concentration in the sample. Spike a second 5-mL sample aliquot with 10 uL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A - B)%/T, where T is the known true value of the spike.

8.7.2.2 Semivolatile organics: Analyze one sample aliquot (extract of 1-L sample) to determine the background concentration (B) of each analyte. If necessary, prepare a new QC check sample concentrate (Section 8.6.1) appropriate for the background concentration in the sample. Spike a second 1-L sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A - B)%/T, where T is the known true value of the spike.

8.7.3 Compare the percent recovery (p) for each analyte with the corresponding criteria presented in the QC Acceptance Criteria Table found at the end of each of the determinative methods. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than the QC check sample concentration (8.6.2), the analyst must use either the QC acceptance criteria presented in the Tables, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte: (1) Calculate accuracy (x') using the equation found in the Method Accuracy and Precision as a Function of Concentration Table (appears at the end of each determinative method), substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in the same Table, substituting x' for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as $(100x'/T) \pm 2.44(100S'/T)\%$.

8.7.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed as described in Section 8.8.

8.8 If any analyte fails the acceptance criteria for recovery in Section 8.7, a QC check standard containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of analytes being simultaneously tested, the

complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes given in a method must be measured in the sample in Section 8.7, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spiked sample.

8.8.1 **Preparation of the QC check standard:** For volatile organics, add 10 uL of the QC check sample concentrate (Section 8.6.1 or 8.7.2) to 5 mL of reagent water. For semivolatile organics, add 1.0 mL of the QC check sample concentrate (Section 8.6.1 or 8.7.2) to 1 L of reagent water. The QC check standard needs only to contain the analytes that failed criteria in the test in Section 8.7. Prepare the QC check standard for analysis following the guidelines given in Method 3500 (e.g., purge-and-trap, extraction, etc.).

8.8.2 Analyzed the QC check standard to determine the concentration measured (A) of each analyte. Calculate each percent recovery (p_s) as 100 (A/T)%, where T is the true value of the standard concentration.

8.8.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in the appropriate Table in each of the methods. Only analytes that failed the test in Section 8.7 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.9 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix type) as in Section 8.7, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p}$ = 90% and s_p = 10%, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.10 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.10.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.10.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (p) and standard deviation of the percent recovery (s) for each of the surrogates.

8.10.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = p + 3s
Lower Control Limit (LCL) = p - 3s

8.10.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Tables A and B of Methods 8240 and 8270, respectively. The limits given in these methods are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Paragraph 8.10.3 must fall within those given in Tables A and B for these matrices.

8.10.5 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.10.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.11 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in the referring analytical methods were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

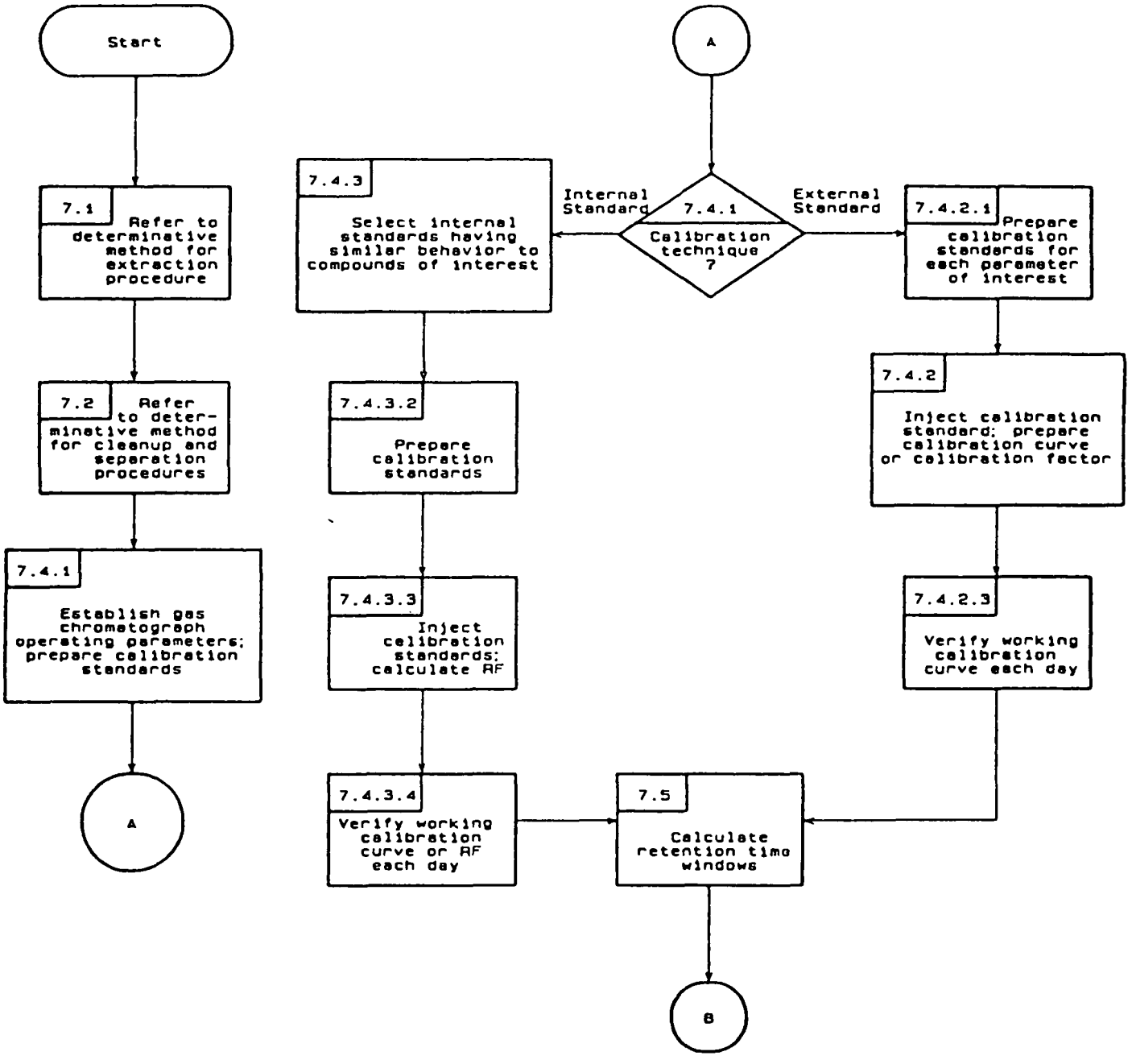
9.2 Refer to the determinative method for specific method performance information.

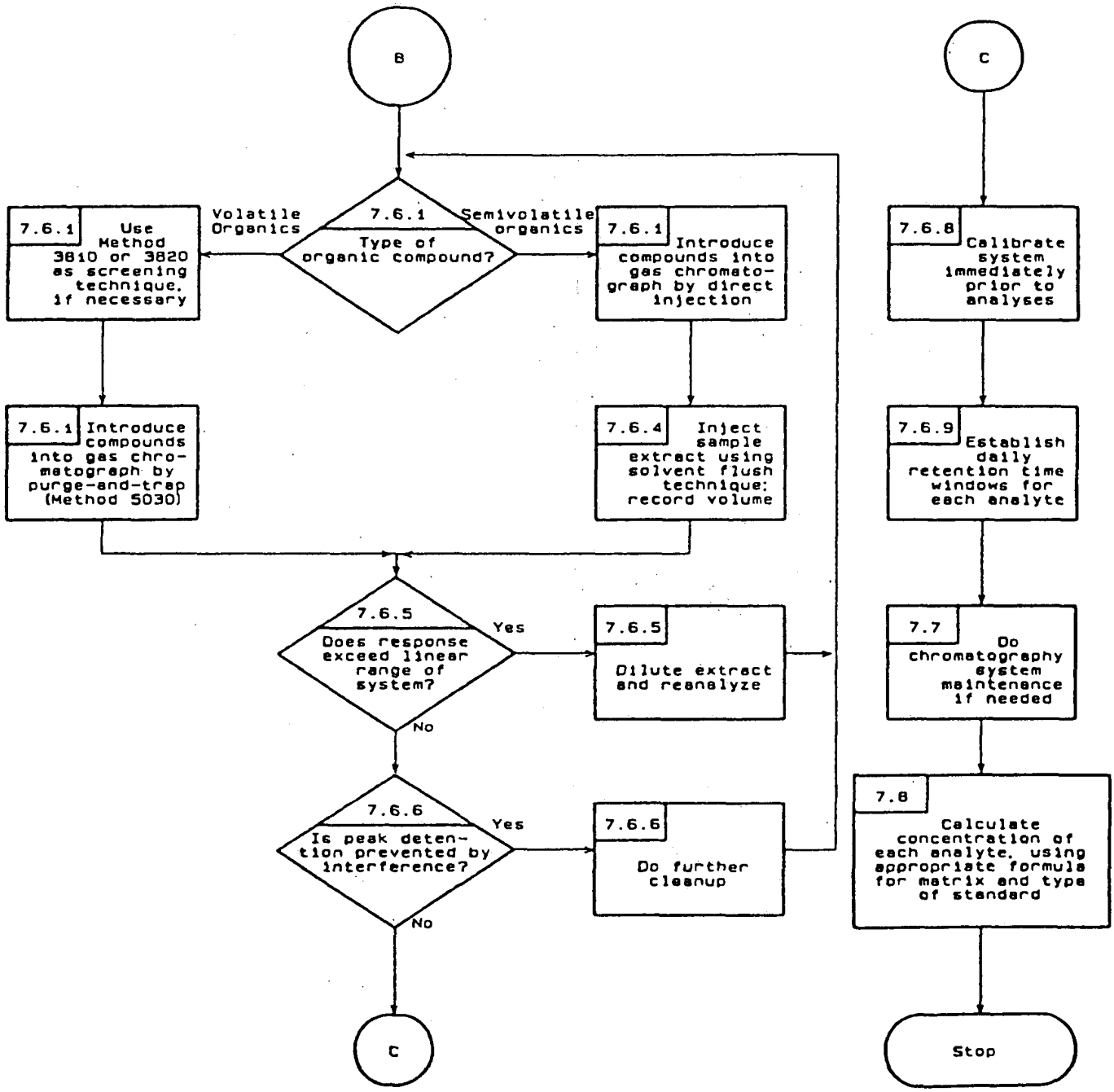
10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

2. U.S. EPA 40 CFR Part 136, Appendix B. "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

3. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.


Start
7.1
Refer to determinative method for extraction procedure
7.2
Refer to determinative method for cleanup and separation procedures
7.4.1
Establish gas chromatograph operating parameters; prepare calibration standards
A
A
7.4.1
Calibration technique ?
Internal Standard
External Standard
7.4.3
Select internal standards having similar behavior to compounds of interest
7.4.3.2
Prepare calibration standards
7.4.3.3
Inject calibration standards; calculate RF
7.4.3.4
Verify working calibration curve or RF each day
7.4.2.1
Prepare calibration standards for each parameter of interest
7.4.2
Inject calibration standard; prepare calibration curve or calibration factor
7.4.2.3
Verify working calibration curve each day
7.5
Calculate retention time windows
B


B
C
7.6.1
Type of organic compound?
Volatile Organics
Semivolatile organics
7.6.1 Use Method 3810 or 3820 as screening technique, if necessary
7.6.1 Introduce compounds into gas chromatograph by direct injection
7.6.8 Calibrate system immediately prior to analyses
7.6.1 Introduce compounds into gas chromatograph by purge-and-trap (Method 5030)
7.6.4 Inject sample extract using solvent flush technique; record volume
7.6.9 Establish daily retention time windows for each analyte
7.6.5
Does response exceed linear range of system?
Yes
No
7.6.5 Dilute extract and reanalyze
7.7 Do chromatography system maintenance if needed
7.6.6
Is peak detention prevented by interference?
Yes
No
7.6.6 Do further cleanup
7.8 Calculate concentration of each analyte, using appropriate formula for matrix and type of standard
C
Stop

METHOD 8010

HALOGENATED VOLATILE ORGANICS

1.0 SCOPE AND APPLICATION

1.1 Method 8010 is used to determine the concentration of various volatile halogenated organic compounds. Table 1 indicates compounds that may be analyzed by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8010 provides gas chromatographic conditions for the detection of halogenated volatile organic compounds. Samples can be analyzed using direct injection or purge-and-trap (Method 5030). Ground water samples must be analyzed using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a halogen-specific detector (HSD).

2.2 The method provides an optional gas chromatographic column that may be helpful in resolving the analytes from interferences that may occur and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Methods 5030 and 8000.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph:

4.1.1 **Gas Chromatograph:** analytical system complete with gas chromatograph suitable for on-column injections or purge-and-trap sample introduction and all required accessories, including detector, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS FOR HALOGENATED VOLATILE ORGANICS

Compound	Retention time (min) Col. 1	Retention time (min) Col. 2	Method detection limit[a] (ug/L)
Benzyl chloride			
Bis(2-chloroethoxy)methane			
Bis(2-chloroisopropyl)ether			
Bromobenzene			
Bromodichloromethane	13.7	14.6	0.10
Bromoform	19.2	19.2	0.20
Bromomethane			
Carbon tetrachloride	13.0	14.4	0.12
Chloroacetaldehyde			
Chlorobenzene	24.2	18.8	0.25
Chloroethane	3.33	8.68	0.52
Chloroform	10.7	12.1	0.05
1-Chlorohexane			
2-Chloroethyl vinyl ether	18.0		0.13
Chloromethane	1.50	5.28	0.08
Chloromethylmethyl ether			
Chlorotoluene			
Dibromochloromethane	16.5	16.6	0.09
Dibromomethane			
1,2-Dichlorobenzene	34.9	23.5	0.15
1,3-Dichlorobenzene	34.0	22.4	0.32
1,4-Dichlorobenzene	35.4	22.3	0.24
Dichlorodifluoromethane			
1,1-Dichloroethane	9.30	12.6	0.07
1,2-Dichloroethane	11.4	15.4	0.03
1,1-Dichloroethylene	8.0	7.72	0.13
trans-1,2-Dichloroethylene	10.1	9.38	0.10
Dichloromethane			
1,2-Dichloropropane	14.9	16.6	0.04
trans-1,3-Dichloropropylene	15.2	16.6	0.34
1,1,2,2-Tetrachloroethane	21.6		0.03
1,1,1,2-Tetrachloroethane			
Tetrachloroethylene	21.7	15.0	0.03
1,1,1-Trichloroethane	12.6	13.1	0.03
1,1,2-Trichloroethane	16.5	18.1	0.02
Trichloroethylene	15.8	13.1	0.12
Trichlorofluoromethane	7.18		
Trichloropropane			
Vinyl chloride	2.67	5.28	0.18

[a] Using purge-and-trap method (Method 5030).

2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

trix	Factor[b]
water	10
vel soil	10
miscible liquid waste	500
evel soil and sludge	1250
ter miscible waste	1250

Sample PQLs are highly matrix-dependent. The PQLs listed herein are rovided for guidance and may not always be achievable.

PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-queous samples, the factor is on a wet-weight basis.

4.1.2 **Columns:**

4.1.2.1 Column 1: 8-ft x 0.1-in I.D. stainless steel or glass column packed with 1% SP-1000 on Carbopack-B 60/80 mesh or equivalent.

4.1.2.2 Column 2: 6-ft x 0.1-in I.D. stainless steel or glass column packed with chemically bonded n-octane on Porasil-C 100/120 mesh (Durapak) or equivalent.

4.1.3 **Detector:** Electrolytic conductivity (HSD).

4.2 Sample introduction apparatus: Refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.3 Syringes: 5-mL Luerlok glass hypodermic and a 5-mL, gas-tight with shutoff valve.

4.4 Volumetric flask: 10-, 50-, 100-, 500-, and 1,000-mL with a ground-glass stopper.

4.5 Microsyringe: 10-, 25-uL with a 0.006-in I.D. needle (Hamilton 702N or equivalent) and a 100-uL.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit (MDL) of the parameters of interest.

5.2 Stock standards: Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials of the toxicity of these materials should be prepared in a hood.

5.2.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.2.2 Add the assayed reference material, as described below.

5.2.2.1 **Liquids:** Using a 100-uL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.2.2.2 **Gases:** To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0-mL mark. Lower the needle to 5 mm above the methanol

meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas rapidly dissolves in the methanol. This may also be accomplished by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.2.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (ug/uL) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.2.5 Prepare fresh standards every 2 months for gases or for reactive compounds such as 2-chloroethylvinyl ether. All other standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

5.3 Secondary dilution standards: Using stock standard solutions, prepare in methanol secondary dilution standards, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 5.4 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.4 Calibration standards: Calibration standards at a minimum of five concentration levels are prepared in reagent water from the secondary dilution of the stock standards. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Each standard should contain each analyte for detection by this method (e.g., some or all of the compounds listed in Table 1 may be included). In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.4.1 Do not inject more than 20 uL of alcoholic standards into 100 mL of reagent water.

5.4.2 Use a 25-uL Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

5.4.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.4.4 Mix aqueous standards by inverting the flask three times only.

5.4.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

5.4.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.4.7 Aqueous standards are not stable and should be discarded after 1 hr, unless properly sealed and stored. The aqueous standards can be stored up to 24 hr, if held in sealed vials with zero headspace.

5.5 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. The compounds recommended for use as surrogate spikes (Paragraph 5.6) have been used successfully as internal standards, because of their generally unique retention times.

5.5.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Section 5.4.

5.5.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.2 and 5.3. It is recommended that the secondary dilution standard be prepared at a concentration of 15 ug/mL of each internal standard compound. The addition of 10 uL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 ug/L.

5.5.3 Analyze each calibration standard according to Section 7.0, adding 10 uL of internal standard spiking solution directly to the syringe.

5.6 Surrogate standards: The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with surrogate halocarbons. A combination of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane is recommended to encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Section 5.2, add a volume to give 750 ug of each surrogate to 45 mL of reagent water contained in a 50-mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/uL. Add 10 uL of this surrogate spiking solution directly into the 5-mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Paragraph 5.5.2).

5.7 Methanol: pesticide quality or equivalent. Store away from other solvents.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-level contaminated soils and sediments. For medium-level soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1:** Set helium gas flow at 40 mL/min flow rate. Set column temperature at 45°C for 3 min; then program an 8°C/min temperature rise to 220°C and hold for 15 min.

7.2.2 **Column 2:** Set helium gas flow at 40 mL/min flow rate. Set column temperature at 50°C for 3 min; then program a 6°C/min temperature rise to 170°C and hold for 4 min.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Paragraph 7.4.1).

7.3.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4 Gas chromatographic analysis:

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap method) or the direct injection method (see Paragraph 7.4.1.1). If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to purging.

7.4.1.1 Direct injection: In very limited applications (e.g., aqueous process wastes) direct injection of the sample into the GC system with a 10-uL syringe may be appropriate. The detection limit is very high (approximately 10,000 ug/L) therefore, it is only

permitted where concentrations in excess of 10,000 ug/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Table 1 summarizes the estimated retention times on the two columns for a number of organic compounds analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1.

7.4.4 Record the sample volume purged or injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Calculation of concentration is covered in Section 7.8 of Method 8000.

7.4.6 If analytical interferences are suspected, or for the purpose of confirmation, analysis using the second GC column is recommended.

7.4.7 If the response for a peak is off-scale, prepare a dilution of the sample with reagent water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

8.2 Mandatory quality control to validate the GC system operation is found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each parameter of interest at a concentration of 10 ug/mL in methanol.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000, Section 8.10).

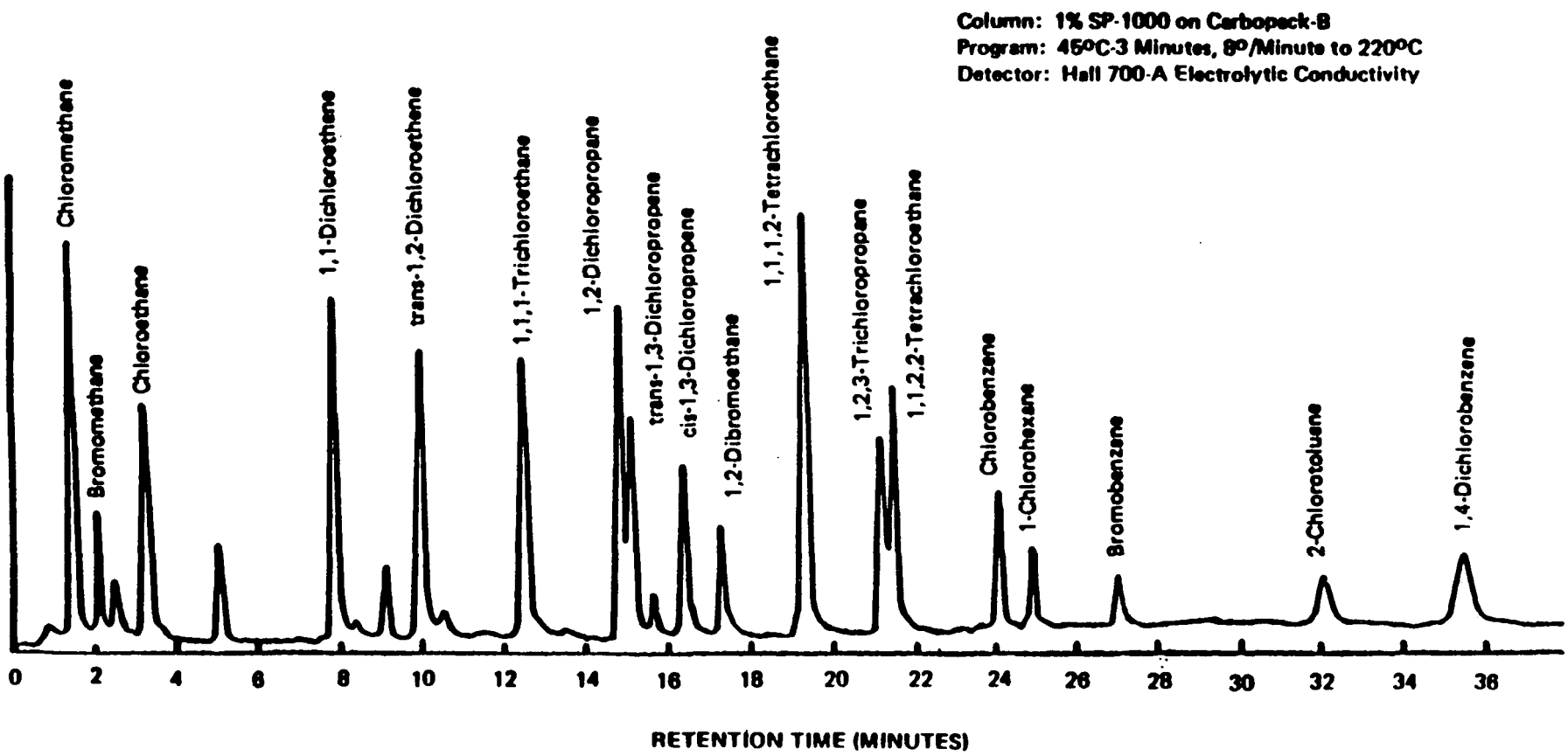


Figure 1. Gas Chromatogram of halogenated volatile organics.

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 This method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 8.0-500 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample introduction technique, and by the calibration procedure used.

10.0 REFERENCES

1. Bellar, T.A., and J.J. Lichtenberg, J. Amer. Water Works Assoc., 66(12), pp. 739-744, 1974.

2. Bellar, T.A., and J.J. Lichtenberg, "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds," in Van Hall, ed., Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp. 108-129, 1979.

3. Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters: Category 11 - Purgeables and Category 12 - Acrolein, Acrylonitrile, and Dichlorodifluoromethane, Report for EPA Contract 68-03-2635 (in preparation).

4. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

5. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

6. "EPA Method Validation Study 23, Method 601 (Purgeable Halocarbons)," Report for EPA Contract 68-03-2856 (in preparation).

TABLE 3. CALIBRATION AND QC ACCEPTANCE CRITERIA[a]

Parameter	Range for Q (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_S (%)
Bromodichloromethane	15.2-24.8	4.3	10.7-32.0	42-172
Bromoform	14.7-25.3	4.7	5.0-29.3	13-159
Bromomethane	11.7-28.3	7.6	3.4-24.5	D-144
Carbon tetrachloride	13.7-26.3	5.6	11.8-25.3	43-143
Chlorobenzene	14.4-25.6	5.0	10.2-27.4	38-150
Chloroethane	15.4-24.6	4.4	11.3-25.2	46-137
2-Chloroethylvinyl ether	12.0-28.0	8.3	4.5-35.5	14-186
Chloroform	15.0-25.0	4.5	12.4-24.0	49-133
Chloromethane	11.9-28.1	7.4	D-34.9	D-193
Dibromochloromethane	13.1-26.9	6.3	7.9-35.1	24-191
1,2-Dichlorobenzene	14.0-26.0	5.5	1.7-38.9	D-208
1,3-Dichlorobenzene	9.9-30.1	9.1	6.2-32.6	7-187
1,4-Dichlorobenzene	13.9-26.1	5.5	11.5-25.5	42-143
1,1-Dichloroethane	16.8-23.2	3.2	11.2-24.6	47-132
1,2-Dichloroethane	14.3-25.7	5.2	13.0-26.5	51-147
1,1-Dichloroethene	12.6-27.4	6.6	10.2-27.3	28-167
trans-1,2-Dichloroethene	12.8-27.2	6.4	11.4-27.1	38-155
1,2-Dichloropropane	14.8-25.2	5.2	10.1-29.9	44-156
cis-1,3-Dichloropropene	12.8-27.2	7.3	6.2-33.8	22-178
trans-1,3-Dichloropropene	12.8-27.2	7.3	6.2-33.8	22-178
Methylene chloride	15.5-24.5	4.0	7.0-27.6	25-162
1,1,2,2-Tetrachloroethane	9.8-30.2	9.2	6.6-31.8	8-184
Tetrachloroethene	14.0-26.0	5.4	8.1-29.6	26-162
1,1,1-Trichloroethane	14.2-25.8	4.9	10.8-24.8	41-138
1,1,2-Trichloroethane	15.7-24.3	3.9	9.6-25.4	39-136
Trichloroethene	15.4-24.6	4.2	9.2-26.6	35-146
Trichlorofluoromethane	13.3-26.7	6.0	7.4-28.1	21-156
Vinyl chloride	13.7-26.3	5.7	8.2-29.9	28-163

Q = Concentration measured in QC check sample, in ug/L.

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_S = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 601 and were calculated assuming a QC check sample concentration of 20 ug/L.

TABLE 4. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Bromodichloromethane	1.12C-1.02	0.11$\bar{X}$+0.04	0.20$\bar{X}$+1.00
Bromoform	0.96C-2.05	0.12$\bar{X}$+0.58	0.21$\bar{X}$+2.41
Bromomethane	0.76C-1.27	0.28$\bar{X}$+0.27	0.36$\bar{X}$+0.94
Carbon tetrachloride	0.98C-1.04	0.15$\bar{X}$+0.38	0.20$\bar{X}$+0.39
Chlorobenzene	1.00C-1.23	0.15$\bar{X}$-0.02	0.18$\bar{X}$+1.21
Chloroethane	0.99C-1.53	0.14$\bar{X}$-0.13	0.17$\bar{X}$+0.63
2-Chloroethyl vinyl ether[b]	1.00C	0.20$\bar{X}$	0.35$\bar{X}$
Chloroform	0.93C-0.39	0.13$\bar{X}$+0.15	0.19$\bar{X}$-0.02
Chloromethane	0.77C+0.18	0.28$\bar{X}$-0.31	0.52$\bar{X}$+1.31
Dibromochloromethane	0.94C+2.72	0.11$\bar{X}$+1.10	0.24$\bar{X}$+1.68
1,2-Dichlorobenzene	0.93C+1.70	0.20$\bar{X}$+0.97	0.13$\bar{X}$+6.13
1,3-Dichlorobenzene	0.95C+0.43	0.14$\bar{X}$+2.33	0.26$\bar{X}$+2.34
1,4-Dichlorobenzene	0.93C-0.09	0.15$\bar{X}$+0.29	0.20$\bar{X}$+0.41
1,1-Dichloroethane	0.95C-1.08	0.08$\bar{X}$+0.17	0.14$\bar{X}$+0.94
1,2-Dichloroethane	1.04C-1.06	0.11$\bar{X}$+0.70	0.15$\bar{X}$+0.94
1,1-Dichloroethene	0.98C-0.87	0.21$\bar{X}$-0.23	0.29$\bar{X}$-0.04
trans-1,2-Dichloroethene	0.97C-0.16	0.11$\bar{X}$+1.46	0.17$\bar{X}$+1.46
1,2-Dichloropropane[b]	1.00C	0.13$\bar{X}$	0.23$\bar{X}$
cis-1,3-Dichloropropene[b]	1.00C	0.18$\bar{X}$	0.32$\bar{X}$
trans-1,3-Dichloropropene[b]	1.00C	0.18$\bar{X}$	0.32$\bar{X}$
Methylene chloride	0.91C-0.93	0.11$\bar{X}$+0.33	0.21$\bar{X}$+1.43
1,1,2,2-Tetrachloroethene	0.95C+0.19	0.14$\bar{X}$+2.41	0.23$\bar{X}$+2.79
Tetrachloroethene	0.94C+0.06	0.14$\bar{X}$+0.38	0.18$\bar{X}$+2.21
1,1,1-Trichloroethane	0.90C-0.16	0.15$\bar{X}$+0.04	0.20$\bar{X}$+0.37
1,1,2-Trichloroethane	0.86C+0.30	0.13$\bar{X}$-0.14	0.19$\bar{X}$+0.67
Trichloroethene	0.87C+0.48	0.13$\bar{X}$-0.03	0.23$\bar{X}$+0.30
Trichlorofluoromethane	0.89C-0.07	0.15$\bar{X}$+0.67	0.26$\bar{X}$+0.91
Vinyl chloride	0.97C-0.36	0.13$\bar{X}$+0.65	0.27$\bar{X}$+0.40

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

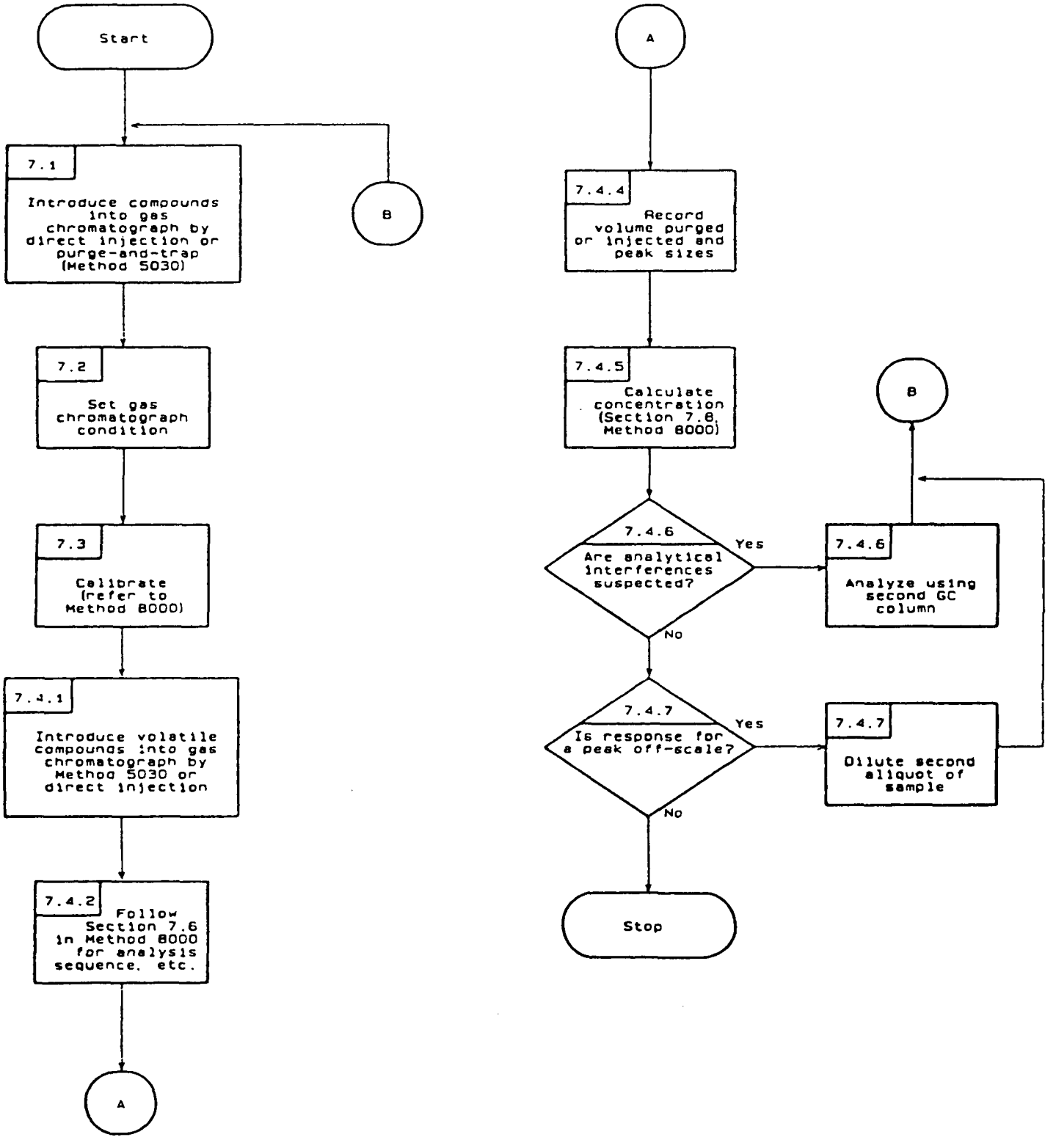
S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.

[a]From 40 CFR Part 136 for Method 601.

[b]Estimates based upon the performance in a single laboratory.


Start
7.1
Introduce compounds into gas chromatograph by direct injection or purge-and-trap (Method 5030)
B
7.2
Set gas chromatograph condition
7.3
Calibrate (refer to Method 8000)
7.4.1
Introduce volatile compounds into gas chromatograph by Method 5030 or direct injection
7.4.2
Follow Section 7.6 in Method 8000 for analysis sequence, etc.
A
A
7.4.4
Record volume purged or injected and peak sizes
7.4.5
Calculate concentration (Section 7.8, Method 8000)
B
7.4.6
Are analytical interferences suspected?
Yes
7.4.6
Analyze using second GC column
No
7.4.7
Is response for a peak off-scale?
Yes
7.4.7
Dilute second aliquot of sample
No
Stop

METHOD 8015

NONHALOGENATED VOLATILE ORGANICS

1.0 SCOPE AND APPLICATION

1.1 Method 8015 is used to determine the concentration of various nonhalogenated volatile organic compounds. Table 1 indicates the compounds that may be investigated by this method.

2.0 SUMMARY OF METHOD

2.1 Method 8015 provides gas chromatographic conditions for the detection of certain nonhalogenated volatile organic compounds. Samples may be analyzed using direct injection or purge-and-trap (Method 5030). Ground water samples must be analyzed by Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a flame ionization detector (FID).

2.2 If interferences are encountered, the method provides an optional gas chromatographic column that may be helpful in resolving the analytes from interferences that may occur and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Method 5030 and 8000.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph:

4.1.1 **Gas Chromatograph:** Analytical system complete with gas chromatograph suitable for on-column injections or purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 **Columns:**

4.1.2.1 Column 1: 8-ft x 0.1-in I.D. stainless steel or glass column packed with 1% SP-1000 on Carbopack-B 60/80 mesh or equivalent.

TABLE 1. NONHALOGENATED VOLATILE ORGANICS

Acrylamide
Diethyl ether
Ethanol
Methyl ethyl ketone (MEK)
Methyl isobutyl ketone (MIBK)
Paraldehyde (trimer of acetaldehyde)

4.1.2.2 Column 2: 6-ft x 0.1-in I.D. stainless steel or glass column packed with n-octane on Porasil-C 100/120 mesh (Durapak) or equivalent.

4.1.3 **Detector:** Flame ionization (FID).

4.2 Sample introduction apparatus: Refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.3 Syringes: A 5-mL Luerlok glass hypodermic and a 5-mL, gas-tight with shutoff valve.

4.4 Volumetric flask: 10-, 50-, 100-, 500-, and 1,000-mL with a ground-glass stopper.

4.5 Microsyringe: 10- and 25-uL with a 0.006-in I.D. needle (Hamilton 702N or equivalent) and a 100-uL.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit (MDL) of the analytes of interest.

5.2 Stock standards: Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids.

5.2.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.2.2 Using a 100-uL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.2.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (ug/uL) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.2.5 Standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

5.3 Secondary dilution standards: Using stock standard solutions, prepare in methanol secondary dilution standards, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 5.4 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.4 Calibration standards: Calibration standards at a minimum of five concentration levels are prepared in reagent water from the secondary dilution of the stock standards. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Each standard should contain each analyte for detection by this method (e.g., some or all of the compounds listed in Table 1 may be included). In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.4.1 Do not inject more than 20 uL of alcoholic standards into 100 mL of reagent water.

5.4.2 Use a 25-uL Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

5.4.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.4.4 Mix aqueous standards by inverting the flask three times only.

5.4.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

5.4.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.4.7 Aqueous standards are not stable and should be discarded after 1 hr, unless properly sealed and stored. The aqueous standards can be stored up to 24 hr, if held in sealed vials with zero headspace.

5.5 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more inter$l standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.5.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Section 5.4.

5.5.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.2 and 5.3. It is recommended that the secondary dilution standard be prepared at a concentration of 15 ug/mL of each internal standard compound. The addition of 10 uL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 ug/L.

5.5.3 Analyze each calibration standard according to Section 7.0, adding 10 uL of internal standard spiking solution directly to the syringe.

5.6 Surrogate standards: The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two surrogate compounds recommended to encompass the range of temperature program used in this method. From stock standard solutions prepared as in Section 5.2, add a volume to give 750 ug of each surrogate to 45 mL of reagent water contained in a 50-mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/uL. Add 10 uL of this surrogate spiking solution directly into the 5-mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Paragraph 5.5.2).

5.7 Methanol: pesticide quality or equivalent. Store away from other solvents.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-level contaminated soils and sediments. For medium-level soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column** 1: Set helium gas flow at 40 mL/min flow rate. Set column temperature at 45°C for 3 min; then program an 8°C/min temperature rise to 220°C and hold for 15 min.

7.2.2 **Column 2:** Set helium gas flow at 40 mL/min flow rate. Set column temperature at 50°C for 3 min; then program a 6°C/min temperature rise to 170°C and hold for 4 min.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Section 7.4.1).

7.3.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4 Gas chromatographic analysis:

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap method) or the direct injection method. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to purging.

7.4.1.1 Direct injection: In very limited applications (e.g., aqueous process wastes), direct injection of the sample into the GC system with a 10 uL syringe may be appropriate. One such application is for verification of the alcohol content of an aqueous sample prior to determining if the sample is ignitable (Methods 1010 or 1020). In this case, it is suggested that direct injection be used. The detection limit is very high (approximately 10,000 ug/L); therefore, it is only permitted when concentrations in excess of 10,000 ug/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Record the sample volume purged or injected and the resulting peak sizes (in area units or peak heights).

7.4.4 Calculation of concentration is covered in Section 7.8 of Method 8000.

7.4.5 If analytical interferences are suspected, or for the purpose of confirmation, analysis using the second GC column is recommended.

7.4.6 If the response for a peak is off-scale, prepare a dilution of the sample with reagent water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

8.2 Mandatory quality control to validate the GC system operation is found in Method 8000, Section 8.6.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 The accuracy and precision obtained will be determined by the sample matrix, sample introduction technique, and calibration procedures used.

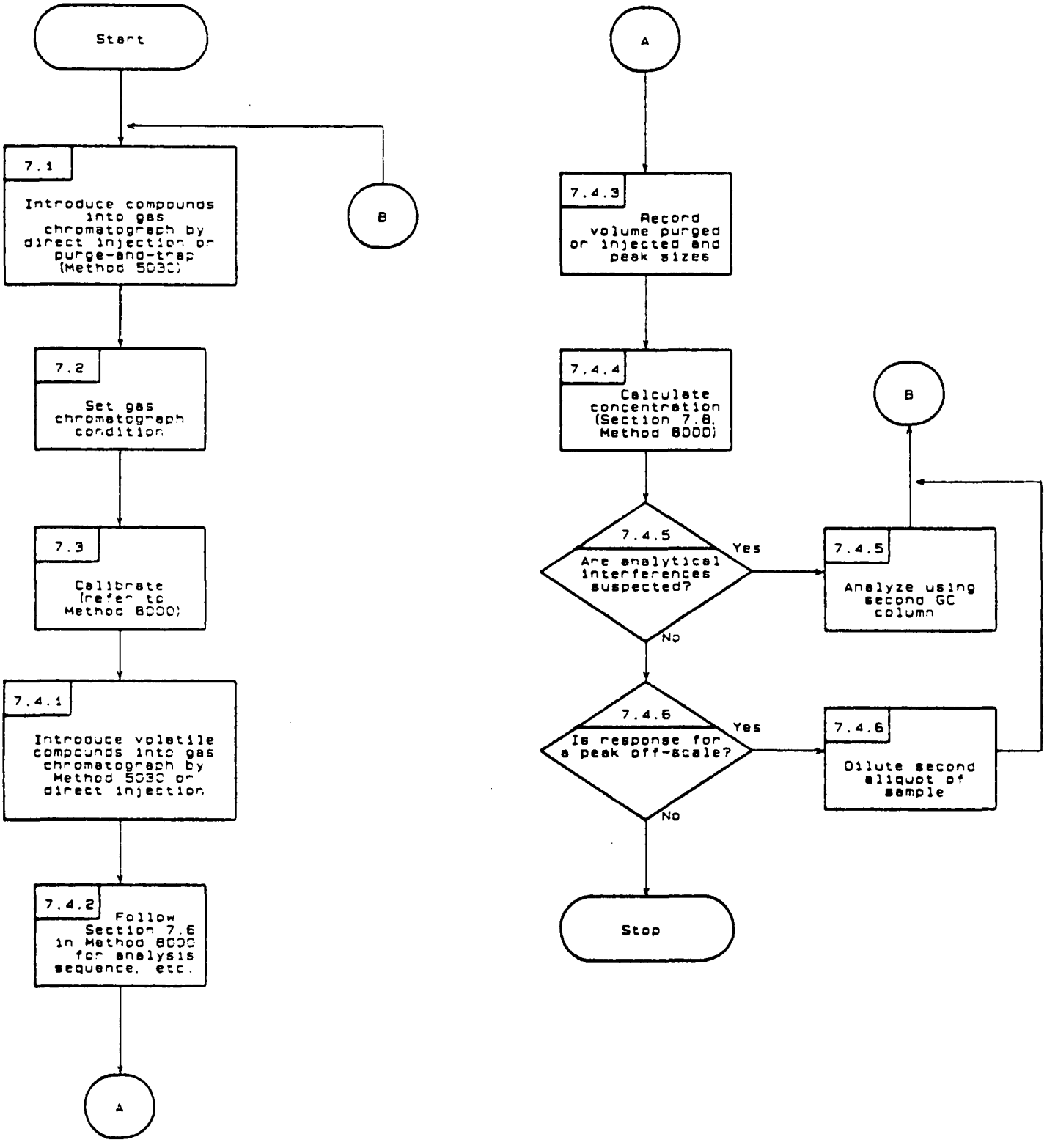
9.2 Specific method performance information will be provided as it becomes available.

10.0 REFERENCES

1. Bellar, T.A., and J.J. Lichtenberg, J. Amer. Water Works Assoc., 66(12), pp. 739-744, 1974.

2. Bellar, T.A., and J.J. Lichtenberg, Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds, in Van Hall, ed., Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp. 108-129, 1979.

3. Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters: Category 11 - Purgeables and Category 12 - Acrolein, Acrylonitrile, and Dichlorodifluoromethane, Report for EPA Contract 68-03-2635 (in preparation).


Start
7.1
Introduce compounds into gas chromatograph by direct injection or purge-and-trap (Method 5030)
B
7.2
Set gas chromatograph condition
7.3
Calibrate (refer to Method 8000)
7.4.1
Introduce volatile compounds into gas chromatograph by Method 5030 or direct injection
7.4.2
Follow Section 7.6 in Method 8000 for analysis sequence, etc.
A
A
7.4.3
Record volume purged or injected and peak sizes
7.4.4
Calculate concentration (Section 7.8, Method 8000)
B
7.4.5
Are analytical interferences suspected?
Yes
7.4.5
Analyze using second GC column
No
7.4.6
Is response for a peak off-scale?
Yes
7.4.6
Dilute second aliquot of sample
No
Stop

METHOD 8020

AROMATIC VOLATILE ORGANICS

1.0 SCOPE AND APPLICATION

1.1 Method 8020 is used to determine the concentration of various aromatic volatile organic compounds. Table 1 indicates compounds which may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8020 provides chromatographic conditions for the detection of aromatic volatile compounds. Samples can be analyzed using direct injection or purge-and-trap (Method 5030). Ground water samples must be determined using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a photo-ionization detector (PID).

2.2 If interferences are encountered, the method provides an optional gas chromatographic column that may be helpful in resolving the analytes from the interferences and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Method 5030 and 8000.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph:

4.1.1 **Gas Chromatograph:** Analytical system complete with gas chromatograph suitable for on-column injections or purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS FOR AROMATIC VOLATILE ORGANICS

Compound	Retention time (min) Col. 1	Retention time (min) Col. 2	Method detection limit[a] (ug/L)
Benzene	3.33	2.75	0.2
Chlorobenzene	9.17	8.02	0.2
1,4-Dichlorobenzene	16.8	16.2	0.3
1,3-Dichlorobenzene	18.2	15.0	0.4
1,2-Dichlorobenzene	25.9	19.4	0.4
Ethyl Benzene	8.25	6.25	0.2
Toluene	5.75	4.25	0.2
Xylenes			

[a] Using purge-and-trap method (Method 5030).

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil	10
Water miscible liquid waste	500
High-level soil and sludge	1250
Non-water miscible waste	1250

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

4.1.2 **Columns:**

4.1.2.1 Column 1: 6-ft x 0.082-in I.D. #304 stainless steel or glass column packed with 5% SP-1200 and 1.75% Bentone-34 on 100/120 mesh Supelcort or equivalent.

4.1.2.2 Column 2: 8-ft x 0.1-in I.D. stainless steel or glass column packed with 5% 1,2,3-Tris(2-cyanoethoxy)propane on 60/80 mesh Chromosorb W-AW or equivalent.

4.1.3 **Detector:** Photoionization (PID) (h-Nu Systems, Inc. Model PI-51-02 or equivalent).

4.2 Sample introduction apparatus: Refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.3 Syringes: A 5-mL Luerlok glass hypodermic and a 5-mL, gas-tight with shutoff valve.

4.4 Volumetric flask: 10-, 50-, 100-, 500-, and 1,000-mL with a ground-glass stopper.

4.5 Microsyringe: 10- and 25-uL with a 0.006-in I.D. needle (Hamilton 702N or equivalent) and a 100-uL.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit (MDL) of the parameters of interest.

5.2 Stock standards: Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids. Because of the toxicity of benzene and 1,4-dichlorobenzene, primary dilutions of these materials should be prepared in a hood.

5.2.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.2.2 Using a 100-uL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.2.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (ug/uL) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction

to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at 4°C and protect from light.

5.2.5 All standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

5.3 Secondary dilution standards: Using stock standard solutions, prepare in methanol secondary dilution standards, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Paragraph 5.4 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.4 Calibration standards: Calibration standards at a minimum of five concentration levels are prepared in reagent water from the secondary dilution of the stock standards. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Each standard should contain each analyte for detection by this method (e.g., some or all of the compounds listed in Table 1 may be included). In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.4.1 Do not inject more than 20 uL of alcoholic standards into 100 mL of reagent water.

5.4.2 Use a 25-uL Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

5.4.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.4.4 Mix aqueous standards by inverting the flask three times only.

5.4.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

5.4.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.4.7 Aqueous standards are not stable and should be discarded after 1 hr, unless properly sealed and stored. The aqueous standards can be stored up to 24 hr, if held in sealed vials with zero headspace.

5.5 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. The compound, alpha,alpha,alpha-trifluorotoluene recommended for use as a surrogate spiking compound (Paragraph 5.6) has been used successfully as an internal standards.

5.5.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Section 5.4.

5.5.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.2 and 5.3. It is recommended that the secondary dilution standard be prepared at a concentration of 15 ug/mL of each internal standard compound. The addition of 10 uL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 ug/L.

5.5.3 Analyze each calibration standard according to Section 7.0, adding 10 uL of internal standard spiking solution directly to the syringe.

5.6 Surrogate standards: The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with surrogate compounds (e.g, alpha,alpha,alpha-trifluorotoluene) recommended to encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Section 5.2, add a volume to give 750 ug of each surrogate to 45 mL of reagent water contained in a 50-mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/uL. Add 10 uL of this surrogate spiking solution directly into the 5-mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Paragraph 5.5.2).

5.7 Methanol: pesticide quality or equivalent. Store away from other solvents.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-level contaminated soils and sediments. For medium-level soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1:** Set helium gas flow at 36 mL/min flow rate. The temperature program sequences are as follows: For lower boiling compounds, operate at 50°C isothermal for 2 min; then program at 6°C/min to 90°C and hold until all compounds have eluted. For higher boiling range of compounds, operate at 50°C isothermal for 2 min; then program at 3°C/min to 110°C and hold until all compounds have eluted. Column 1 provides outstanding separations for a wide variety of aromatic hydrocarbons. Column 1 should be used as the primary analytical column because of its unique ability to resolve para-, meta-, and ortho-aromatic isomers.

7.2.2 **Column 2:** Set helium gas flow at 30 mL/min flow rate. The temperature program sequence is as follows: 40°C isothermal for 2 min; then 2°C/min to 100°C and hold until all compounds have eluted. Column 2, an extremely high-polarity column, has been used for a number of years to resolve aromatic hydrocarbons from alkanes in complex samples. However, because resolution between some of the aromatics is not as efficient as with Column 1, Column 2 should be used as a confirmatory column.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Section 7.4.1).

7.3.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4 Gas chromatographic analysis:

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap method) or the direct injection method. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to purging.

7.4.1.1 Direct injection: In very limited applications (e.g., aqueous process wastes), direct injection of the sample into the GC system with a 10 uL syringe may be appropriate. The detection limit is very high (approximately 10,000 ug/L); therefore, it is only permitted when concentrations in excess of 10,000 ug/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.4.2 Follow Section 7.6 of Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Table 1 summarizes the estimated retention times and detection limits for a number of organic compounds analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1. Figure 2 shows an example of the separation achieved using Column 2.

7.4.4 Record the sample volume purged or injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Calculation of concentration is covered in Section 7.8 of Method 8000.

7.4.6 If analytical interferences are suspected, or for the purpose of confirmation, analysis using the second GC column is recommended.

7.4.7 If the response for a peak is off-scale, prepare a dilution of the sample with reagent water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

8.2 Mandatory quality control to validate the GC system operation is found in Method 8000, Section 8.6.

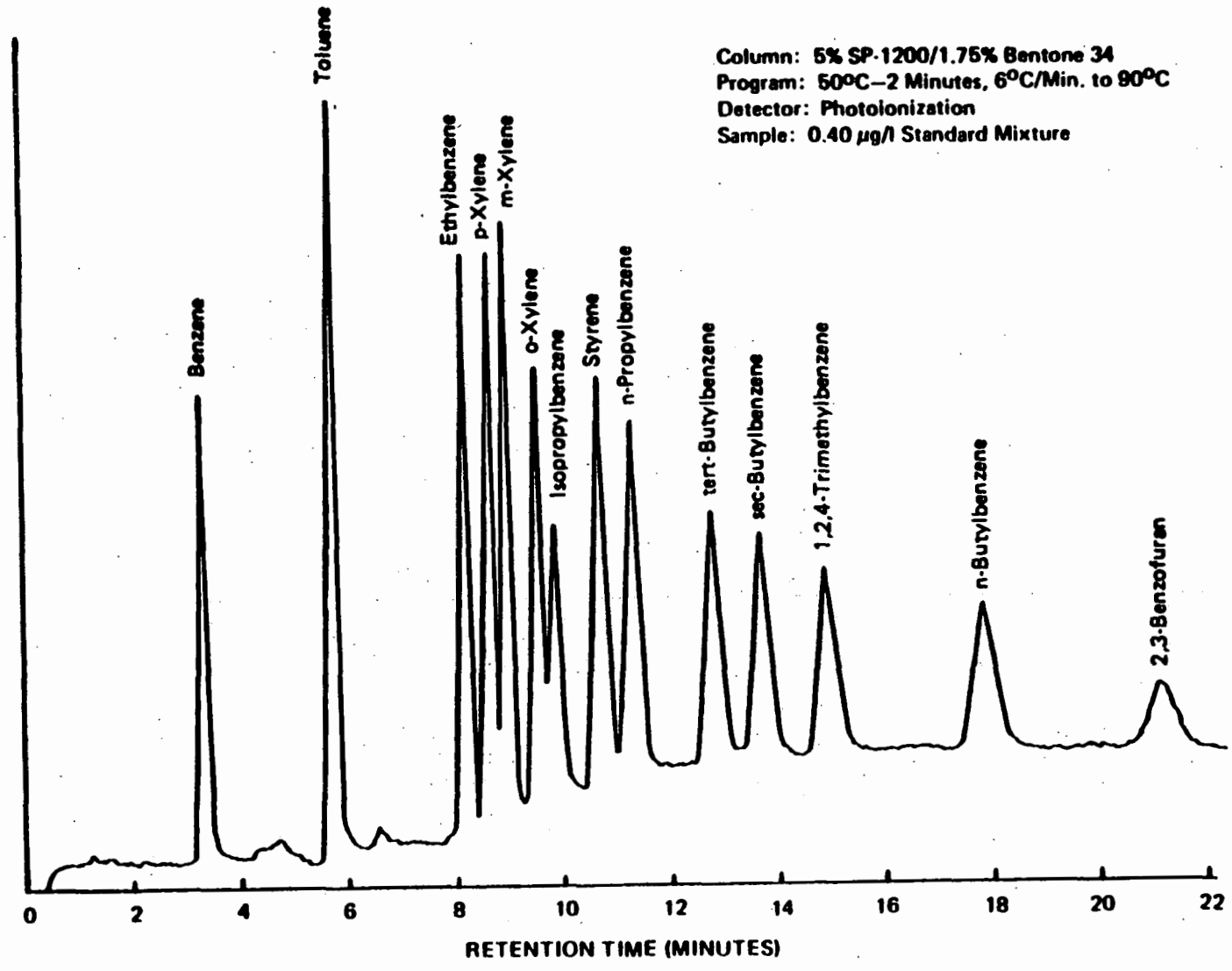


Figure 1. Chromatogram of aromatic volatile organics (column 1 conditions).

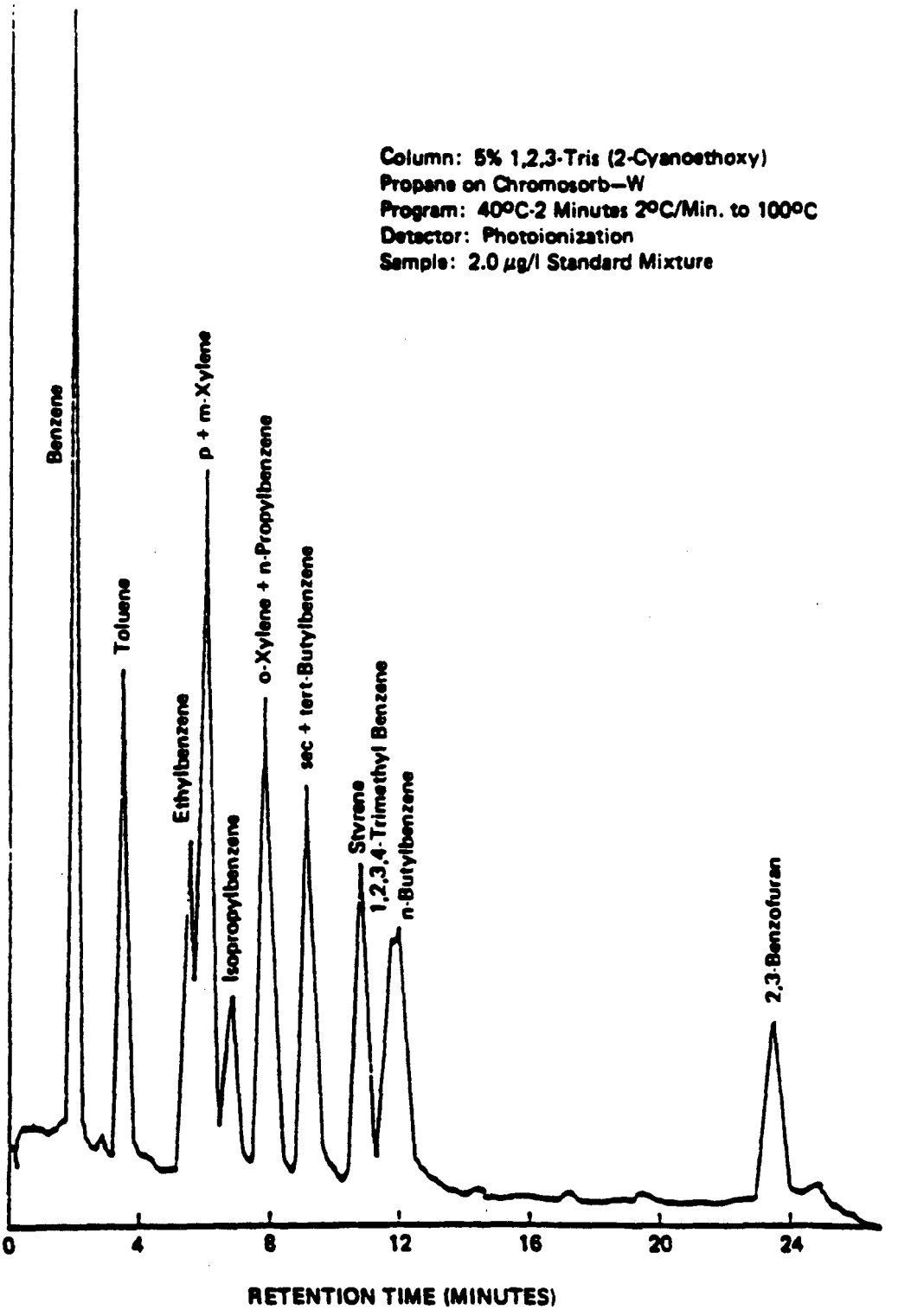


Figure 2. Chromatogram of aromatic volatile organics (column 2 conditions).

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each parameter of interest at a concentration of 10 ug/mL in methanol.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 This method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 2.1-500 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample introduction technique, and by the calibration procedure used.

10.0 REFERENCES

1. Bellar, T.A., and J.J. Lichtenberg, J. Amer. Water Works Assoc., 66(12), pp. 739-744, 1974.

2. Bellar, T.A., and J.J. Lichtenberg, Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds, in Van Hall (ed.), Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp. 108-129, 1979.

3. Dowty, B.J., S.R. Antoine, and J.L. Laseter, "Quantitative and Qualitative Analysis of Purgeable Organics by High Resolution Gas Chromatography and Flame Ionization Detection," in Van Hall, ed., Measurement of Organic Pollutants in Water and Wastewater. ASTM STP 686, pp. 24-35, 1979.

4. Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 11 - Purgeables and Category 12 - Acrolein, Acrylonitrile, and Dichlorodifluoromethane. Report for EPA Contract 68-03-2635 (in preparation).

5. "EPA Method Validation Study 24, Method 602 (Purgeable Aromatics)," Report for EPA Contract 68-03-2856 (in preparation).

6. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

7. Provost, L.P., and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

TABLE 3. CALIBRATION AND QC ACCEPTANCE CRITERIA[a]

Parameter	Range for Q (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_S (%)
Benzene	15.4-24.6	4.1	10.0-27.9	39-150
Chlorobenzene	16.1-23.9	3.5	12.7-25.4	55-135
1,2-Dichlorobenzene	13.6-26.4	5.8	10.6-27.6	37-154
1,3-Dichlorobenzene	14.5-25.5	5.0	12.8-25.5	50-141
1,4-Dichlorobenzene	13.9-26.1	5.5	11.6-25.5	42-143
Ethylbenzene	12.6-27.4	6.7	10.0-28.2	32-160
Toluene	15.5-24.5	4.0	11.2-27.7	46-148

Q = Concentration measured in QC check sample, in ug/L.

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_S = Percent recovery measured.

[a]Criteria are from 40 CFR Part 136 for Method 602 and were calculated assuming a QC check sample concentration of 20 ug/L. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 1.

TABLE 4. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Benzene	0.92C+0.57	0.09$\bar{X}$+0.59	0.21$\bar{X}$+0.56
Chlorobenzene	0.95C+0.02	0.09$\bar{X}$+0.23	0.17$\bar{X}$+0.10
1,2-Dichlorobenzene	0.93C+0.52	0.17$\bar{X}$-0.04	0.22$\bar{X}$+0.53
1,3-Dichlorobenzene	0.96C-0.04	0.15$\bar{X}$-0.10	0.19$\bar{X}$+0.09
1,4-Dichlorobenzene	0.93C-0.09	0.15$\bar{X}$+0.28	0.20$\bar{X}$+0.41
Ethylbenzene	0.94C+0.31	0.17$\bar{X}$+0.46	0.26$\bar{X}$+0.23
Toluene	0.94C+0.65	0.09$\bar{X}$+0.48	0.18$\bar{X}$-0.71

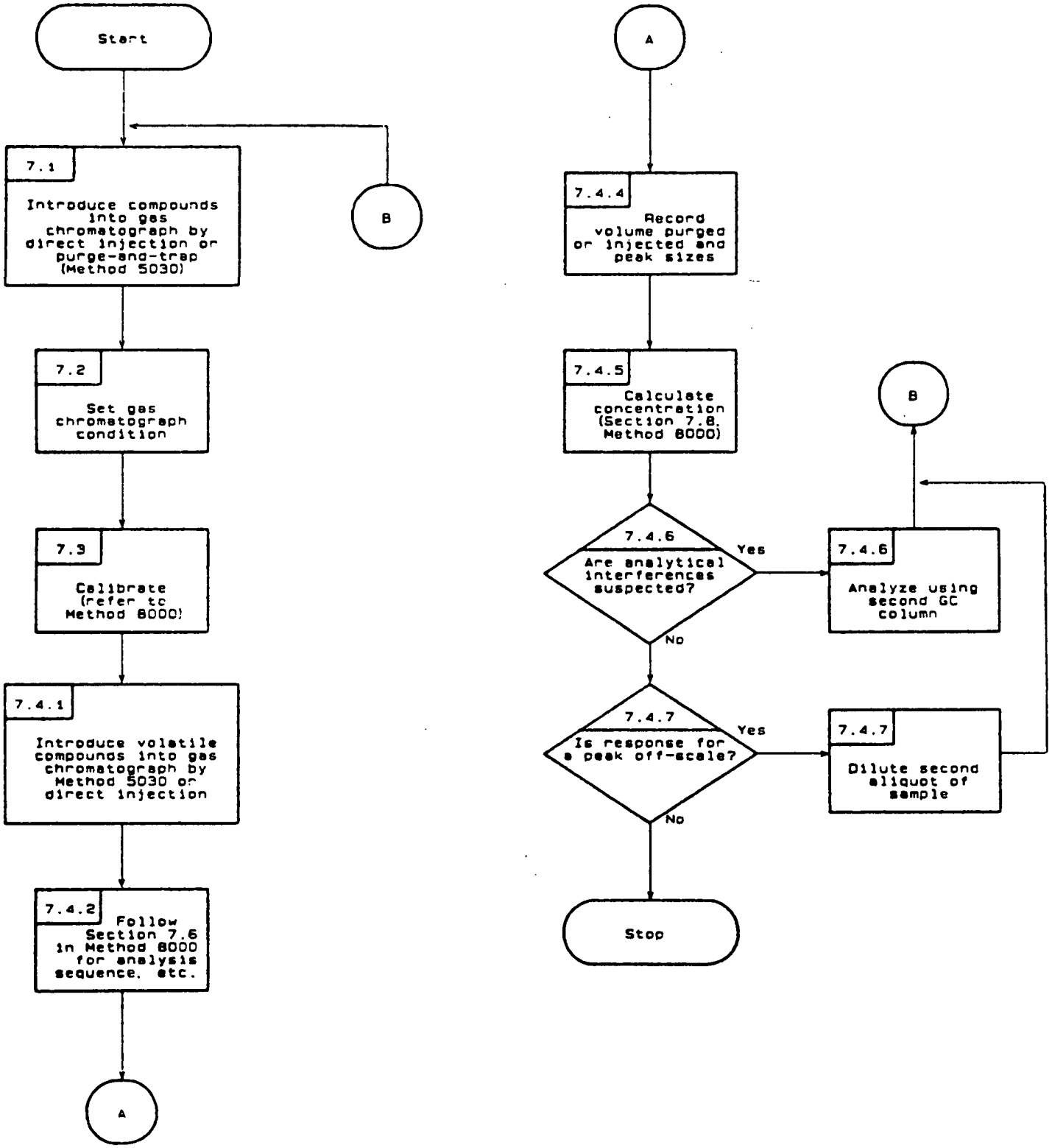
x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.


Start
7.1
Introduce compounds into gas chromatograph by direct injection or purge-and-trap (Method 5030)
B
7.2
Set gas chromatograph condition
7.3
Calibrate (refer to Method 8000)
7.4.1
Introduce volatile compounds into gas chromatograph by Method 5030 or direct injection
7.4.2
Follow Section 7.6 in Method 8000 for analysis sequence, etc.
A
A
7.4.4
Record volume purged or injected and peak sizes
7.4.5
Calculate concentration (Section 7.8, Method 8000)
B
7.4.6
Are analytical interferences suspected?
Yes
7.4.6
Analyze using second GC column
No
7.4.7
Is response for a peak off-scale?
Yes
7.4.7
Dilute second aliquot of sample
No
Stop

METHOD 8030

ACROLEIN, ACRYLONITRILE, ACETONITRILE

1.0 SCOPE AND APPLICATION

1.1 Method 8030 is used to determine the concentration of the following three volatile organic compounds:

Acrolein (Propenal)
Acrylonitrile
Acetonitrile

1.2 Table 1 lists chromatographic conditions and method detection limits for acrolein and acrylonitrile in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8030 provides gas chromatographic conditions for the detection of the three volatile organic compounds. Samples can be analyzed using direct injection or purge-and-trap (Method 5030). Ground water samples must be analyzed using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a flame ionization detector (FID).

2.2 The method provides an optional gas chromatographic column that may be helpful in resolving the analytes from interferences that may occur and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Methods 5030 and 8000.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph:

4.1.1 **Gas Chromatograph:** Analytical system complete with gas chromatograph suitable for on-column injections or purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak height and/or peak area is recommended.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Compound	Retention time (min) Col. 1	Retention time (min) Col. 2	Method detection limit[a] (ug/L)
Acrolein	10.6	8.2	0.7
Acrylonitrile	12.7	9.8	0.5

[a] Based on using purge-and-trap, Method 5030.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil	10
Water miscible liquid waste	500
High-level soil and sludge	1250
Non-water miscible waste	1250

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

4.1.2 **Columns:**

4.1.2.1 Column 1: 10-ft x 2-mm I.D. stainless steel or glass packed with Porapak-QS (80/100 mesh) or equivalent.

4.1.2.2 Column 2: 6-ft x 0.1-in I.D. stainless steel or glass packed with Chromosorb 101 (60/80 mesh) or equivalent.

4.1.3 **Detector:** Flame ionization (FID).

4.2 Sample introduction apparatus: Refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.3 Syringes: A 5-mL Luerlok glass hypodermic and a 5-mL, gas-tight with shutoff valve.

4.4 Volumetric flask: 10-, 50-, 100-, 500-, and 1,000-mL with a ground-glass stopper.

4.5 Microsyringe: 10- and 25-uL with a 0.006-in I.D. needle (Hamilton 702N or equivalent) and a 100-uL.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit (MDL) of the parameters of interest.

5.2 Stock standards: Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids. Because acrolein and acrylonitrile are lachrymators, primary dilutions of these compounds should be prepared in a hood.

5.2.1 Place about 9.8 mL of reagent water in a 10-mL tared ground-glass-stoppered volumetric flask. For acrolein standards the reagent water must be adjusted to pH 4-5 using hydrochloric acid (1:1) or sodium hydroxide (10 N), if necessary. Weigh the flask to the nearest 0.1 mg.

5.2.2 Using a 100-uL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the water without contacting the neck of the flask.

5.2.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (ug/uL) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at 4°C and protect from light.

5.2.5 Prepare fresh standards daily.

5.3 Secondary dilution standards: Using stock standard solutions, prepare in reagent water secondary dilution standards, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Paragraph 5.4 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.4 Calibration standards: Calibration standards at a minimum of five concentration levels are prepared in reagent water from the secondary dilution of the stock standards. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Each standard should contain each analyte for detection by this method. In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.4.1 Use a 25-uL Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of standards into water).

5.4.2 Never use pipets to dilute or transfer samples or aqueous standards.

5.4.3 These standards must be prepared daily.

5.5 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.5.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Section 5.4.

5.5.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.2 and 5.3. It is recommended that the secondary dilution standard be prepared at a concentration of 15 ug/mL of each internal standard compound. The addition of 10 uL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 ug/L.

5.5.3 Analyze each calibration standard according to Section 7.0, adding 10 uL of internal standard spiking solution directly to the syringe.

5.6 Surrogate standards: The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two surrogate compounds (e.g., compounds similar in analytical behavior to the analytes of interest but which are not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Section 5.2, add a volume to give 750 ug of each surrogate to 45 mL of reagent water contained in a 50-mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/uL. Add 10 uL of this surrogate spiking solution directly into the 5-mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Paragraph 5.5.2).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-level contaminated soils and sediments. For high-level soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1:** Set helium gas flow at 30 mL/min flow rate. Set column temperature at 110°C for 1.5 min; then heat as rapidly as possible to 150°C and hold for 20 min.

7.2.2 **Column 2:** Set helium gas flow at 40 mL/min flow rate. Set column temperature at 80°C for 4 min; then program at 50°C/min to 120°C and hold for 12 min.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Section 7.4.1).

7.3.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4 Gas chromatographic analysis:

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap method) or the direct injection method. If the internal standard calibration technique is used, add 10 uL of the internal standard to the sample prior to purging.

7.4.1.1 Direct injection: In very limited applications (e.g., aqueous process wastes), direct injection of the sample into the GC system with a 10 uL syringe may be appropriate. The detection limit is very high (approximately 10,000 ug/L); therefore, it is only permitted when concentrations in excess of 10,000 ug/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.4.2 Follow Section 7.6 of Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Table 1 summarizes the estimated retention times and detection limits for a number of organic compounds analyzable using this method. Figure 1 illustrates the chromatographic separation of acrolein and of acrylonitrile using Column 1.

7.4.4 Record the sample volume purged or injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Calculation of concentration is covered in Section 7.8 of Method 8000.

7.4.6 If analytical interferences are suspected, or for the purpose of confirmation, analysis using the second GC column is recommended.

7.4.7 If the response for a peak is off-scale, prepare a dilution of the sample with reagent water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

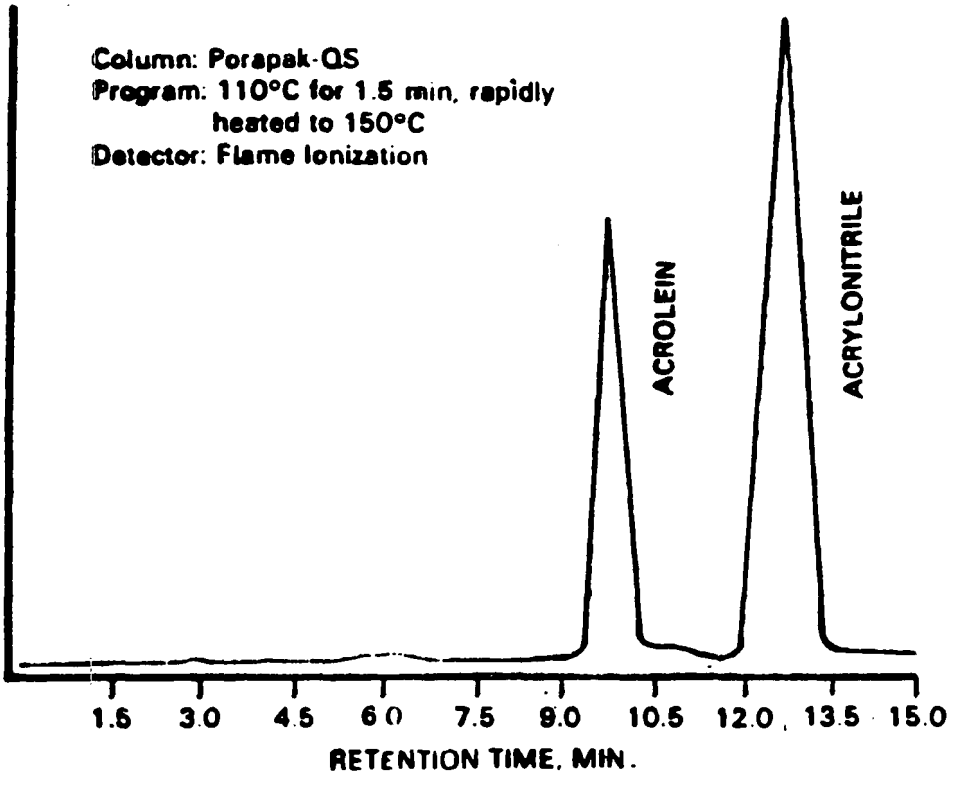


Figure 1. Gas chromatogram of acrolein and acrylonitrile.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each parameter of interest at a concentration of 25 ug/mL in reagent water.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives single laboratory accuracy and precision for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 In a single laboratory, the average recoveries and standard deviations presented in Table 4 were obtained using Method 5030. Seven replicate samples were analyzed at each spike level.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample introduction technique, and by the calibration procedure used.

10.0 REFERENCES

1. Bellar, T.A. and J.J. Lichtenberg, J. Amer. Water Works Assoc., 66(12), pp. 739-744, 1974.

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3. Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters, Category 11: Purgeables and Category 12: Acrolein, Acrylonitrile, and Dichlorodifluoromethane, Report for EPA Contract 68-03-2635 (in preparation).

4. Going, J., et al., Environmental Monitoring Near Industrial Sites - Acrylonitrile, Office of Toxic Substances, U.S. EPA, Washington, DC, EPA 560/6-79-003, 1979.

5. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

6. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

7. Kerns, E.H., et al. "Determination of Acrolein and Acrylonitrile in Water by Heated Purge and Trap Technique," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, 1980.

8. "Evaluation of Method 603," Final Report for EPA Contract 68-03-1760 (in preparation).

TABLE 3. CALIBRATION AND QC ACCEPTANCE CRITERIA[a]

Parameter	Range for Q (ug/L)	Limit for S (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_S (%)
Acrolein	45.9-54.1	4.6	42.9-60.1	88-118
Acrylonitrile	41.2-58.8	9.9	33.1-69.9	71-135

Q = Concentration measured in QC check sample, in ug/L.

S = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

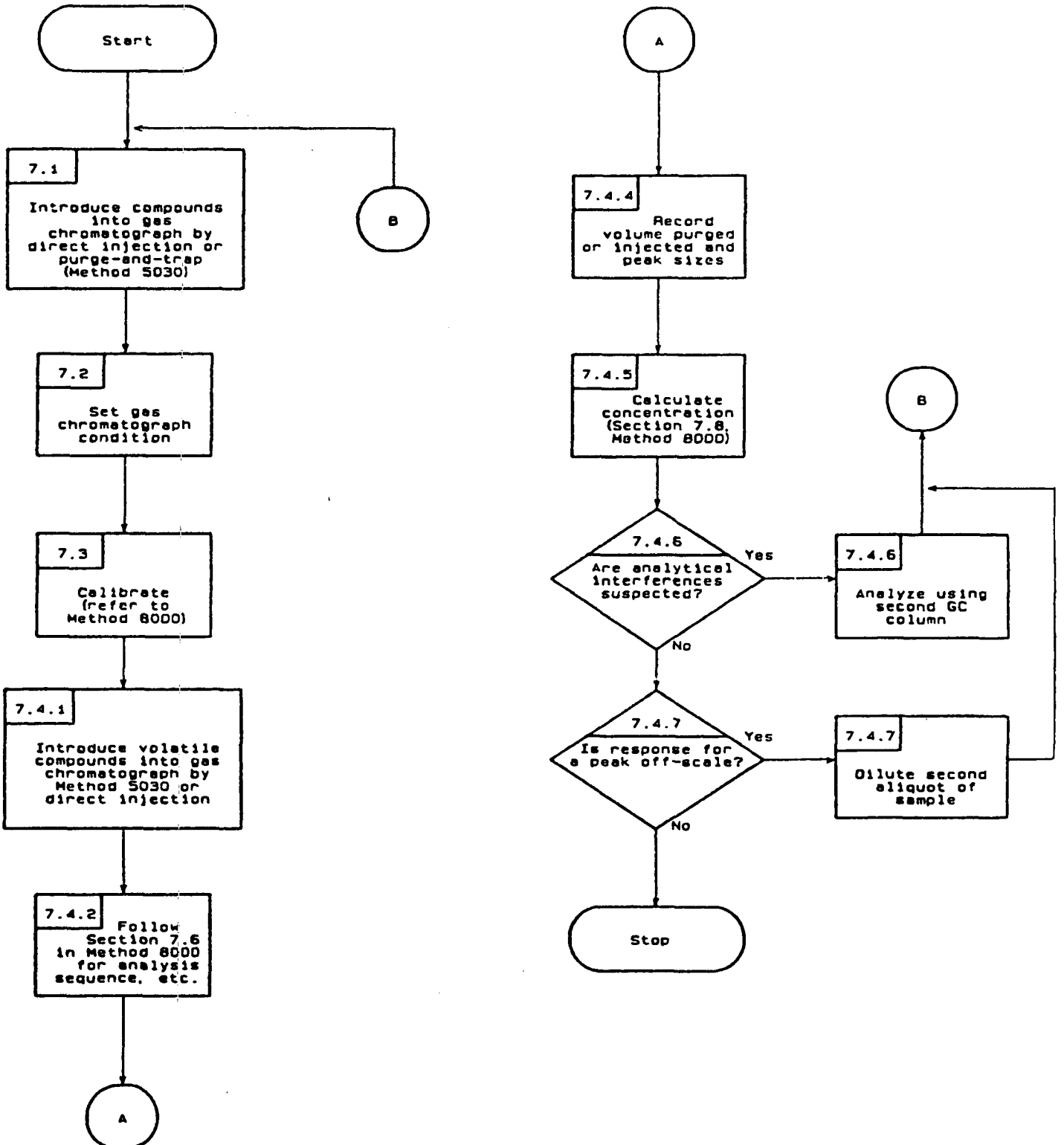
P, P_S = Percent recovery measured.

[a]Criteria from 40 CFR Part 136 for Method 603 and were calculated assuming a QC check sample concentration of 50 ug/L.

TABLE 4. SINGLE LABORATORY ACCURACY AND PRECISION

Parameter	Spike conc. (ug/L)	Average recovery (ug/L)	Standard deviation (ug/L)	Average percent recovery	Sample matrix[a]
Acrolein	5.0	5.2	0.2	104	RW
	50.0	51.4	0.7	103	RW
	5.0	4.0	0.2	80	POTW
	50.0	44.4	0.8	89	POTW
	5.0	0.1	0.1	2	IW
	100.0	9.3	1.1	9	IW
Acrylonitrile	5.0	4.2	0.2	84	RW
	50.0	51.4	1.5	103	RW
	20.0	20.1	0.8	100	POTW
	100.0	101.3	1.5	101	POTW
	10.0	9.1	0.8	91	IW
	100.0	104.0	3.2	104	IW

[a]RW = Reagent water.
POTW = Prechlorination secondary effluent from a municipal sewage treatment plant.
IW = Industrial wastewater containing an unidentified acrolein reactant.


Start
7.1
Introduce compounds into gas chromatograph by direct injection or purge-and-trap (Method 5030)
B
7.2
Set gas chromatograph condition
7.3
Calibrate (refer to Method 8000)
7.4.1
Introduce volatile compounds into gas chromatograph by Method 5030 or direct injection
7.4.2
Follow Section 7.6 in Method 8000 for analysis sequence, etc.
A
A
7.4.4
Record volume purged or injected and peak sizes
7.4.5
Calculate concentration (Section 7.8, Method 8000)
7.4.6
Are analytical interferences suspected?
Yes
No
7.4.6
Analyze using second GC column
B
7.4.7
Is response for a peak off-scale?
Yes
No
7.4.7
Dilute second aliquot of sample
Stop

METHOD 8040

PHENOLS

1.0 SCOPE AND APPLICATION

1.1 Method 8040 is used to determine the concentration of various phenolic compounds. Table 1 indicates compounds that may be analyzed by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8040 provides gas chromatographic conditions for the detection of phenolic compounds. Prior to analysis, samples must be extracted using appropriate techniques (see Chapter Two for guidance). Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL sample is injected into a gas chromatograph using the solvent flush technique, and compounds in the GC effluent are detected by a flame ionization detector (FID).

2.2 Method 8040 also provides for the preparation of pentafluorobenzyl-bromide (PFB) derivatives, with additional cleanup procedures for electron capture gas chromatography. This is to reduce detection limits of some phenols and to aid the analyst in the elimination of interferences.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.3 Interferences coextracted from samples will vary considerably from source to source, depending upon the waste being sampled. Although general cleanup techniques are recommended as part of this method, unique samples may require additional cleanup.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph:

4.1.1 **Gas Chromatograph:** Analytical system complete with gas chromatograph suitable for on-column injections and all required

TABLE 1. FLAME IONIZATION GAS CHROMATOGRAPHY OF PHENOLS

Compound	Retention time (min)	Method Detection limit (ug/L)
2-sec-Butyl-4,6-dinitrophenol (DNBP)		
4-Chloro-3-methylphenol	7.50	0.36
2-Chlorophenol	1.70	0.31
Cresols (methyl phenols)		
2-Cyclohexyl-4,6-dinitrophenol		
2,4-Dichlorophenol	4.30	0.39
2,6-Dichlorophenol		
2,4-Dimethylphenol	4.03	0.32
2,4-Dinitrophenol	10.00	13.0
2-Methyl-4,6-dinitrophenol	10.24	16.0
2-Nitrophenol	2.00	0.45
4-Nitrophenol	24.25	2.8
Pentachlorophenol	12.42	7.4
Phenol	3.01	0.14
Tetrachlorophenols		
Trichlorophenols		
2,4,6-Trichlorophenol	6.05	0.64

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.2 **Columns:**

4.1.2.1 Column for underivatized phenols: 1.8-m x 2.0-mm I.D. glass column packed with 1% SP-1240DA on Supelcoport 80/100 mesh or equivalent.

4.1.2.2 Column for derivatized phenols: 1.8-m x 2-mm I.D. glass column packed with 5% OV-17 on Chromosorb W-AW-DMCS 80/100 mesh or equivalent.

4.1.3 **Detectors:** Flame ionization (FID) and electron capture (ECD).

4.2 Reaction vial: 20-mL, with Teflon-lined cap.

4.3 Volumetric flask: 10-, 50-, and 100-mL, ground-glass stopper.

4.4 Kuderna-Danish (K-D) apparatus:

4.4.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts

4.4.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.4.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.4.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.5 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.6 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.7 Microsyringe: 10-uL.

4.8 Syringe: 5-mL.

5.0 REAGENTS

5.1 Solvents: Hexane, 2-propanol, and toluene (pesticide quality or equivalent).

5.2 Derivatization reagent: Add 1 mL pentafluorobenzyl bromide and 1 g 18-crown-6-ether to a 50-mL volumetric flask and dilute to volume with 2-propanol. Prepare fresh weekly. This operation should be carried out in a hood. Store at 4°C and protect from light.

5.2.1 **Pentafluorobenzyl bromide** (alpha-Bromopentafluorotoluene): 97% minimum purity.
NOTE: This chemical is a lachrymator.

5.2.2 **18-crown-6-ether** (1,4,7,10,13,16-Hexaoxacyclooctadecane): 98% minimum purity.
NOTE: This chemical is highly toxic.

5.3 Potassium carbonate: (ACS) Powdered.

5.4 Stock standard solutions:

5.4.1 Prepare stock standard solution at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in 2-propanol and diluting to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.4.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.4.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.5 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared through dilution of the stock standards with 2-propanol. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

5.6 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.6.1 Prepare calibration standards at a minimum of five concentrations for each analyte as described in Paragraph 5.5.

5.6.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with 2-propanol.

5.6.3 Analyze each calibration standard according to Section 7.0.

5.7 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (if necessary), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with phenolic surrogates (e.g., 2-fluorophenol and 2,4,6-tribromophenol) recommended to encompass the range of the temperature program used in this method. Method 3500, Section 5.3.1.1, details instructions on the preparation of acid surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a pH of less than or equal to 2 with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550. Extracts obtained from application of either Method 3540 or 3550 should undergo Acid-Base Partition Cleanup, using Method 3650.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to 2-propanol. The exchange is performed during the micro K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.2.2 Increase the temperature of the hot water bath to 95-100°C. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of 2-propanol. A 5-mL syringe is recommended for this operation. Add one or two clean boiling chips to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding about 0.5 mL of 2-propanol to the top. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water.

Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 2.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. Add an additional 2 mL of 2-propanol , add one or two clean boiling chips to the concentrator tube, and resume concentrating as before. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.2.3 Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of 2-propanol. Adjust the extract volume to 1.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. If the extract requires no further derivatization or cleanup, proceed with gas chromatographic analysis.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column for underivatized phenols:** Set nitrogen gas flow at 30 mL/min flow rate. Set column temperature at 80°C and immediately program an 8°C/min temperature rise to 150°C; hold until all compounds have eluted.

7.2.2 **Column for derivatized phenols:** Set 5% methane/95% argon gas flow at 30 mL/min flow rate. Set column temperature at 200°C isothermal.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used for the underivatized phenols. Refer to Method 8000 for a description of each of these procedures. If derivatization of the phenols is required, the method of external calibration should be used by injecting five or more levels of calibration standards that have also undergone derivatization and cleanup prior to instrument calibration.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.4.2 Phenols are to be determined on a gas chromatograph equipped with a flame ionization detector according to the conditions listed for the 1% SP-1240DA column (Paragraph 7.2.1). Table 1 summarizes estimated

retention times and sensitivities that should be achieved by this method for clean water samples. Practical quantitation limits for other matrices are list in Table 2.

7.4.3 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.4 An example of a GC/FID chromatogram for certain phenols is shown in Figure 1. Other packed or capillary (open-tubular) columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

7.4.5 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.6 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Section 7.8 of Method 8000 for calculation equations.

7.4.7 If peak detection using the SP-1240DA column with the flame ionization detector is prevented by interferences, PFB derivatives of the phenols should be analyzed on a gas chromatograph equipped with an electron capture detector according to the conditions listed for the 5% OV-17 column (Paragraph 7.2.2). The derivatization and cleanup procedure is outlined in Sections 7.5 through 7.6. Table 3 summarizes estimated retention times for derivatives of some phenols using the conditions of this method.

7.4.8 Figure 2 shows a GC/ECD chromatogram of PFB derivatives of certain phenols.

7.4.9 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.10 Determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. The method of external calibration should be used (see Method 8000 for guidance). The concentration of the individual compounds in the sample is calculated as follows.

$$\text{Concentration (ug/L)} = [(A)(V_t)(B)(D)]/[(V_i)(X)(C)(E)]$$

where:

A = Mass of underivatized phenol represented by area of peak in sample chromatogram, determined from calibration curve (see Method 8000 Paragraph 7.4.2), ng.

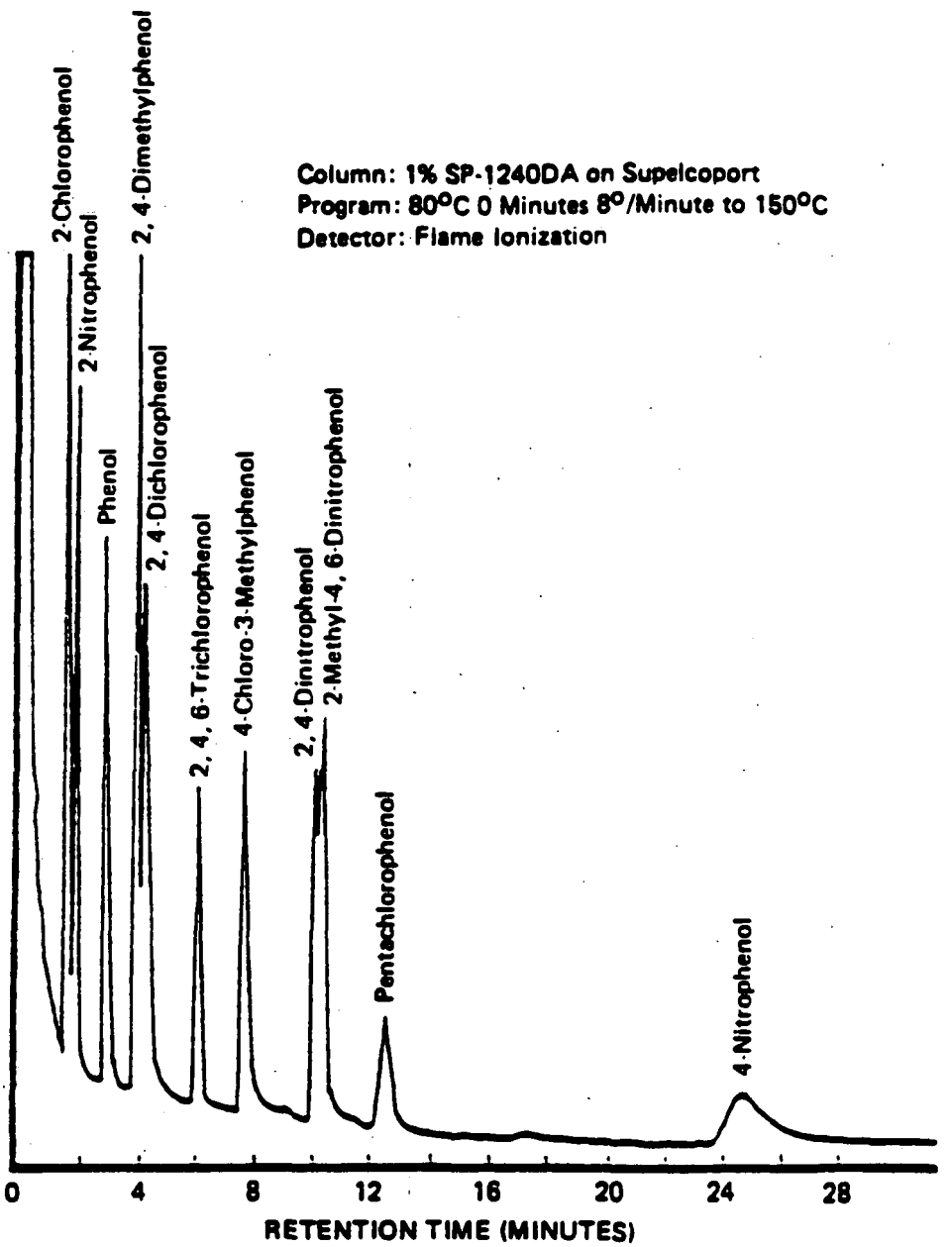


Figure 1. Gas chromatogram of phenols.

TABLE 3. ELECTRON CAPTURE GAS CHROMATOGRAPHY OF PFB DERIVATIVES

Parent compound	Retention time (min)	Method detection limit (ug/L)
4-Chloro-2-methylphenol	4.8	1.8
2-Chlorophenol	3.3	0.58
2,4-Dichlorophenol	5.8	0.68
2,4-Dimethylphenol	2.9	0.63
2,4-Dinitrophenol	46.9	
2-Methyl-4,6-dinitrophenol	36.6	
2-Nitrophenol	9.1	0.77
4-Nitrophenol	14.0	0.70
Pentachlorophenol	28.8	0.59
Phenol	1.8	2.2
2,4,6-Trichlorophenol	7.0	0.58

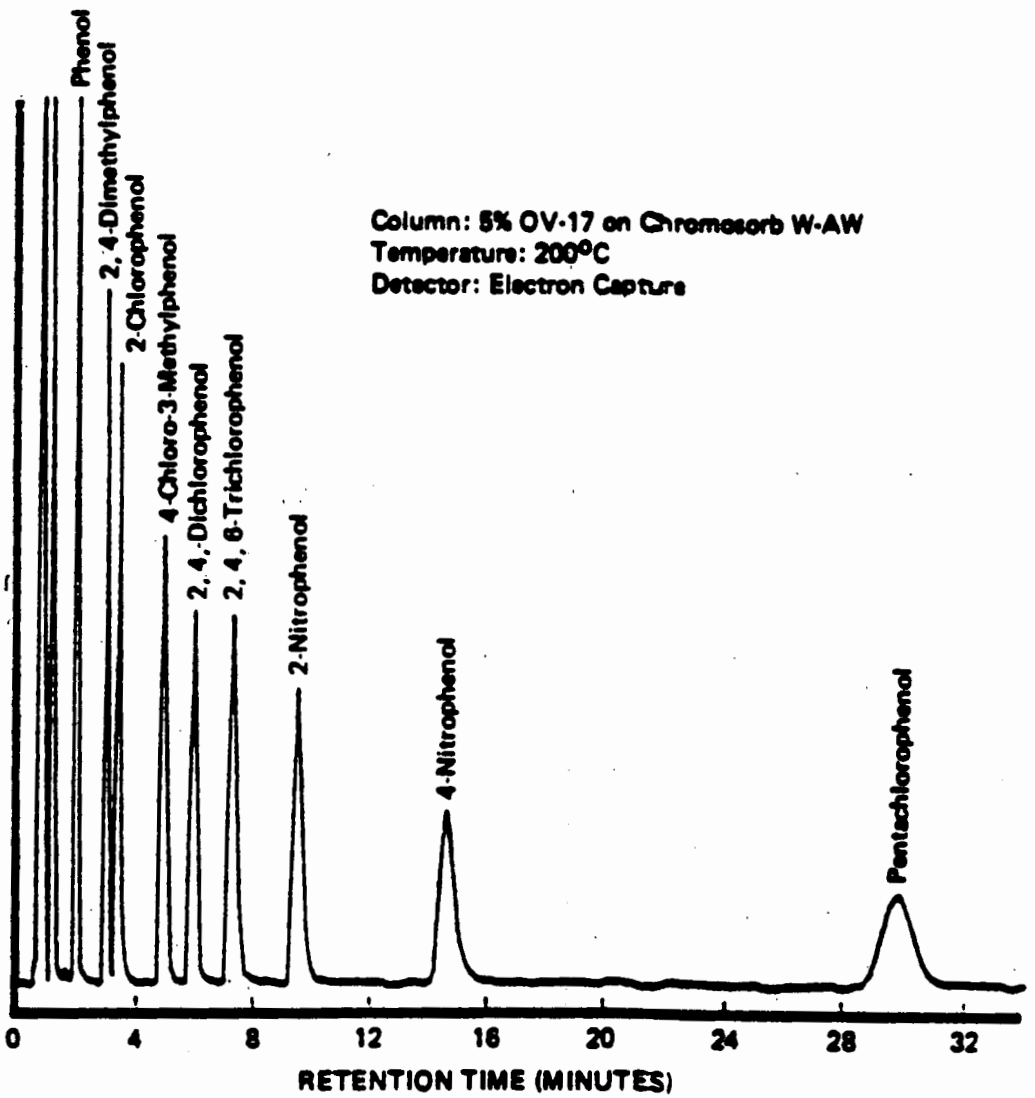


Figure 2. Gas chromatogram of PFB derivatives of phenols.

V_t = Total amount of column eluate or combined fractions from which V_i was taken, uL.

B = Total volume of hexane added in Paragraph 7.5.5, mL.

D = Total volume of 2-propanol extract prior to derivatization, mL.

V_i = Volume injected, uL.

X = Volume of water extracted, mL, or weight of nonaqueous sample extracted, g, from Section 7.1. Either the dry or wet weight of the nonaqueous sample may be used, depending upon the specific application of the data.

C = Volume of hexane sample solution added to cleanup column (Method 3630, Section 7.2), mL.

E = Volume of 2-propanol extract carried through derivatization in Paragraph 7.5.1, mL.

7.5 Derivatization: If interferences prevent measurement of peak area during analysis of the extract by flame ionization gas chromatography, the phenols must be derivatized and analyzed by electron capture gas chromatography.

7.5.1 Pipet a 1.0-mL aliquot of the 2-propanol stock standard solution or of the sample extract into a glass reaction vial. Add 1.0 mL derivatization reagent (Paragraph 5.3). This amount of reagent is sufficient to derivatize a solution whose total phenolic content does not exceed 0.3 mg/mL.

7.5.2 Add approximately 3 mg of potassium carbonate to the solution and shake gently.

7.5.3 Cap the mixture and heat it for 4 hr at 80°C in a hot water bath.

7.5.4 Remove the solution from the hot water bath and allow it to cool.

7.5.5 Add 10 mL hexane to the reaction vial and shake vigorously for 1 min. Add 3.0 mL distilled, deionized water to the reaction vial and shake for 2 min.

7.5.6 Decant the organic layer into a concentrator tube and cap with a glass stopper. Proceed with cleanup procedure.

7.6 Cleanup:

7.6.1 Cleanup of the derivatized extracts takes place using Method 3630 (Silica Gel Cleanup), in which specific instructions for cleanup of the derivatized phenols appear.

7.6.2 Following column cleanup, analyze the samples using GC/ECD, as described starting in Paragraph 7.4.7.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method used. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each analyte of interest at a concentration of 100 ug/mL in 2-propanol.

8.2.2 Table 4 indicates the calibration and QC acceptance criteria for this method. Table 5 gives method accuracy and precision as functions of concentration for the analytes. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 The method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 12 to 450 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 5.

9.2 The accuracy and precision obtained will be affected by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

1. Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 3 - Chlorinated Hydrocarbons and Category 8 - Phenols. Report for EPA Contract 68-03-2625 (in preparation).

2. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

3. "Determination of Phenols in Industrial and Municipal Wastewaters," Report for EPA Contract 68-03-2625 (in preparation).

4. "EPA Method Validation Study Test Method 604 (Phenols)," Report for EPA Contract 68-03-2625 (in preparation).

5. Kawarahara, F.K. "Microdetermination of Derivatives of Phenols and Mercaptans by Means of Electron Capture Gas Chromatography," Analytical Chemistry, 40, 1009, 1968.

6. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

7. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

TABLE 4. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_S (%)
4-Chloro-3-methylphenol	100	16.6	56.7-113.4	99-122
2-Chlorophenol	100	27.0	54.1-110.2	38-126
2,4-Dichlorophenol	100	25.1	59.7-103.3	44-119
2,4-Dimethylphenol	100	33.3	50.4-100.0	24-118
4,6-Dinitro-2-methylphenol	100	25.0	42.4-123.6	30-136
2,4-Dinitrophenol	100	36.0	31.7-125.1	12-145
2-Nitrophenol	100	22.5	56.6-103.8	43-117
4-Nitrophenol	100	19.0	22.7-100.0	13-110
Pentachlorophenol	100	32.4	56.7-113.5	36-134
Phenol	100	14.1	32.4-100.0	23-108
2,4,6-Trichlorophenol	100	16.6	60.8-110.4	53-119

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_S = Percent recovery measured.

[a]Criteria from 40 CFR Part 136 for Method 604. These criteria are based directly upon the method performance data in Table 5. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 5.

TABLE 5. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
4-Chloro-3-methylphenol	0.87C-1.97	0.11$\bar{X}$-0.21	0.16$\bar{X}$+1.41
2-Chlorophenol	0.83C-0.84	0.18$\bar{X}$+0.20	0.21$\bar{X}$+0.75
2,4-Dichlorophenol	0.81C+0.48	0.17$\bar{X}$-0.02	0.18$\bar{X}$+0.62
2,4-Dimethylphenol	0.62C-1.64	0.30$\bar{X}$-0.89	0.25$\bar{X}$+0.48
4,6-Dinitro-2-methylphenol	0.84C-1.01	0.15$\bar{X}$+1.25	0.19$\bar{X}$+5.85
2,4-Dinitrophenol	0.80C-1.58	0.27$\bar{X}$-1.15	0.29$\bar{X}$+4.51
2-Nitrophenol	0.81C-0.76	0.15$\bar{X}$+0.44	0.14$\bar{X}$+3.84
4-Nitrophenol	0.46C+0.18	0.17$\bar{X}$+2.43	0.19$\bar{X}$+4.79
Pentachlorophenol	0.83C+2.07	0.22$\bar{X}$-0.58	0.23$\bar{X}$+0.57
Phenol	0.43C+0.11	0.20$\bar{X}$-0.88	0.17$\bar{X}$+0.77
2,4,6-Trichlorophenol	0.86C-0.40	0.10$\bar{X}$+0.53	0.13$\bar{X}$+2.40

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

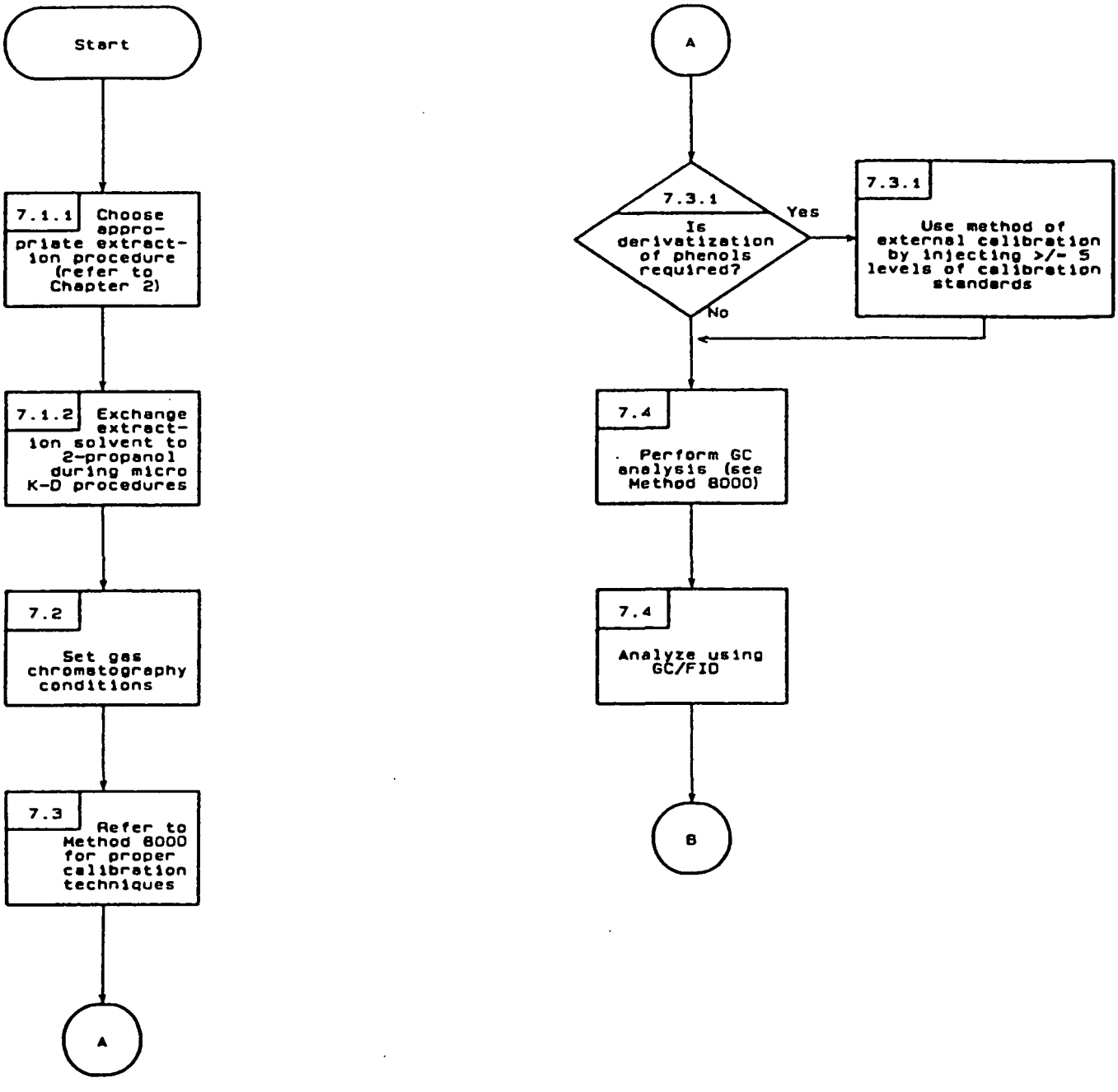
s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

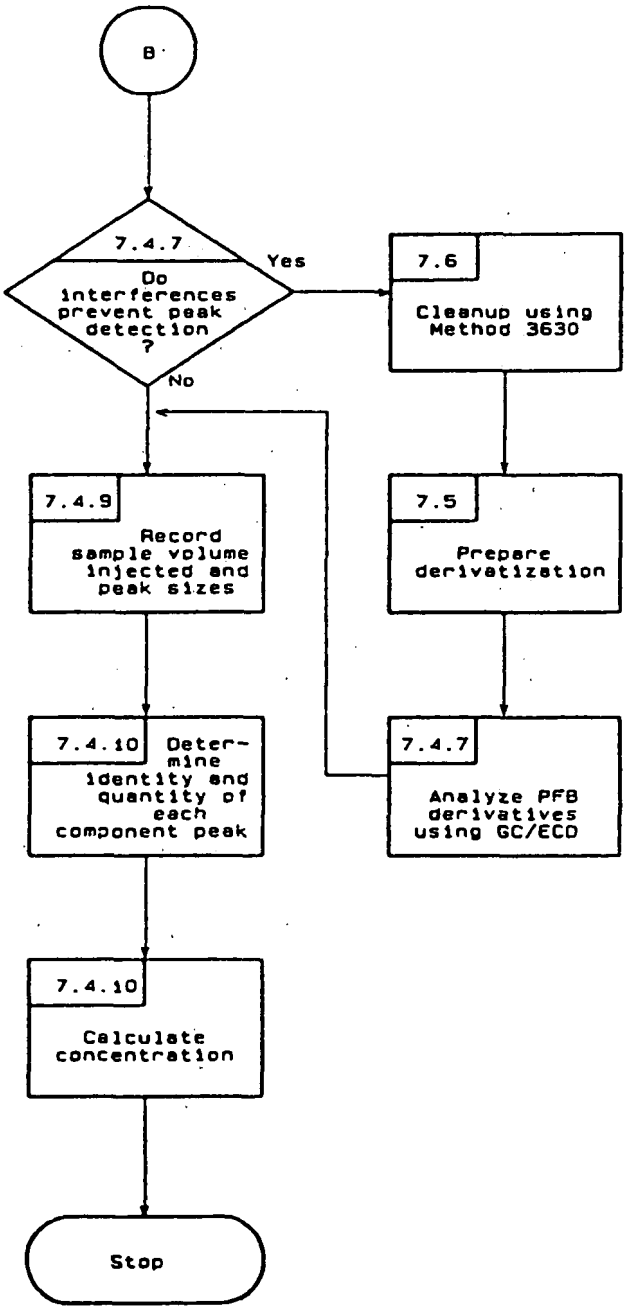
S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.

[a]From 40 CFR Part 136 for Method 604.


Start
7.1.1 Choose appropriate extraction procedure (refer to Chapter 2)
7.1.2 Exchange extraction solvent to 2-propanol during micro K-D procedures
7.2 Set gas chromatography conditions
7.3 Refer to Method 8000 for proper calibration techniques
A
A
7.3.1 Is derivatization of phenols required?
Yes
No
7.3.1 Use method of external calibration by injecting >/- 5 levels of calibration standards
7.4 Perform GC analysis (see Method 8000)
7.4 Analyze using GC/FID
B


B
7.4.7
Do interferences prevent peak detection ?
Yes
No
7.6
Cleanup using Method 3630
7.4.9
Record sample volume injected and peak sizes
7.5
Prepare derivatization
7.4.10
Deter-mine identity and quantity of each component peak
7.4.7
Analyze PFB derivatives using GC/ECD
7.4.10
Calculate concentration
Stop

METHOD 8060

PHTHALATE ESTERS

1.0 SCOPE AND APPLICATION

1.1 Method 8060 is used to determine the concentration of various phthalate esters. Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8060 provides gas chromatographic conditions for the detection of ppb levels of phthalate esters. Prior to use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL aliquot of the extract is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or a flame ionization detector (FID). Ground water samples should be determined by ECD.

2.2 The method provides a second gas chromatographic column that may be helpful in resolving the analytes from interferences that may occur and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Phthalate esters contaminate many types of products commonly found in the laboratory. The analyst must demonstrate that no phthalate residues contaminate the sample or solvent extract under the conditions of analysis. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

3.3 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.4 Interferences coextracted from samples will vary considerably from source to source, depending upon the waste being sampled. Although general cleanup techniques are recommended as part of this method, unique samples may require additional cleanup.

TABLE 1. RETENTION TIME AND DETECTION LIMIT INFORMATION FOR PHTHALATE ESTERS

Compound	Retention time (min) Col. 1[a]	Retention time (min) Col. 2[b]	Method detection limit (ug/L) ECD	Method detection limit (ug/L) FID
Benzyl butyl phthalate	*6.94	**5.11	0.34	15
Bis(2-ethylhexyl)phthalate	*8.92	**10.5	2.0	20
Di-n-butyl phthalate	8.65	3.50	0.36	14
Diethyl phthalate	2.82	1.27	0.49	31
Dimethyl phthalate	2.03	0.95	0.29	19
Di-n-octyl phthalate	*16.2	**8.0	3.0	31

[a]Column 1: Supelcoport 100/120 mesh coated with 1.5% SP-2250/1.95% SP-2401 packed in a 180-cm x 4-mm I.D. glass column with carrier gas at 60 mL/min flow rate. Column temperature is 180°C, except where * indicates 220°C. Under these conditions the retention time of Aldrin is 5.49 min at 180°C and 1.84 min at 220°C.

[b]Column 2: Supelcoport 100/120 mesh with 3% OV-1 in a 180-cm x 4-mm I.D. glass column with carrier gas at 60 mL/min flow rate. Column temperature is 200°C, except where ** indicates 220°C. Under these conditions the retention time of Aldrin is 3.18 min at 200°C and 1.46 min at 220°C.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph:

4.1.1 **Gas chromatograph:** Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.2 **Columns:**

4.1.2.1 Column 1: 1.8-m x 4-mm I.D. glass column packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport 100/120 mesh or equivalent.

4.1.2.2 Column 2: 1.8-m x 4-mm I.D. glass column packed with 3% OV-1 on Supelcoport 100/120 mesh or equivalent.

4.1.3 **Detectors:** Flame ionization (FID) or electron capture (ECD).

4.2 Volumetric flask: 10-, 50-, and 100-mL, ground-glass stopper.

4.3 Kuderna-Danish (K-D) apparatus:

4.3.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts

4.3.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.3.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.6 Microsyringe: 10-uL.

4.7 Syringe: 5-mL.

4.8 Vials: Glass, 2- and 20-mL capacity with Teflon-lined screw cap.

5.0 REAGENTS

5.1 Solvents: Hexane, acetone, isooctane (2,2,4-trimethylpentane) (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in isooctane and diluting to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared through dilution of the stock standards with isooctane. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.4 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each

sample, standard, and reagent water blank with one or two surrogates (e.g., phthalates that are not expected to be in the sample) recommended to encompass the range of the temperature program used in this method. Method 3500, Section 5.3.1.1, details instructions on the preparation of base/neutral surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.2.2 Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. The extract will be handled differently at this point, depending on whether or not cleanup is needed. If cleanup is not required, proceed to Paragraph 7.1.2.3. If cleanup is needed, proceed to Paragraph 7.1.2.4.

7.1.2.3 If cleanup of the extract is not required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5-mL syringe is recommended for this operation. Adjust the extract volume to

10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with gas chromatographic analysis.

7.1.2.4 If cleanup of the extract is required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with a minimum amount of hexane. A 5-mL syringe is recommended for this operation. Add a clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding about 0.5 mL of hexane to the top. Place the micro-K-D apparatus on the water bath (80°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.2.5 Remove the micro-Snyder column and rinse the flask and its lower joint into the concentrator tube with 0.2 mL of hexane. Adjust the extract volume to 2.0 mL and proceed with either Method 3610 or 3620.

7.2 Gas chromatography conditions (Recommended): The analysis for phthalate esters may be conducted using either a flame ionization or an electron capture detector. The ECD may, however, provide substantially better sensitivity.

7.2.1 **Column 1:** Set 5% methane/95% argon carrier gas flow at 60 mL/min flow rate. Set column temperature at 180°C isothermal.

7.2.2 **Column 2:** Set 5% methane/95% argon carrier gas flow at 60 mL/min flow rate. Set column temperature at 200°C isothermal.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 If cleanup is performed on the samples, the analyst should process a series of standards through the cleanup procedure and then analyze the samples by GC. This will confirm elution patterns and the absence of interferents from the reagents.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Examples of GC/ECD chromatograms for phthalate esters are shown in Figures 1 and 2.

7.4.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each analyte peak in the sample chromatogram. See Section 7.8 of Method 8000 for calculation equations.

7.4.6 If peak detection and identification are prevented due to interferences, the hexane extract may undergo cleanup using either Method 3610 or 3620.

7.5 Cleanup:

7.5.1 Proceed with either Method 3610 or 3620, using the 2-mL hexane extracts obtained from Paragraph 7.1.2.5.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each analyte of interest at the following concentrations in acetone: butyl benzyl phthalate, 10 ug/mL; bis(2-ethylhexyl) phthalate, 50 ug/mL; di-n-octyl phthalate, 50 ug/mL; and any other phthalate, 25 ug/mL.

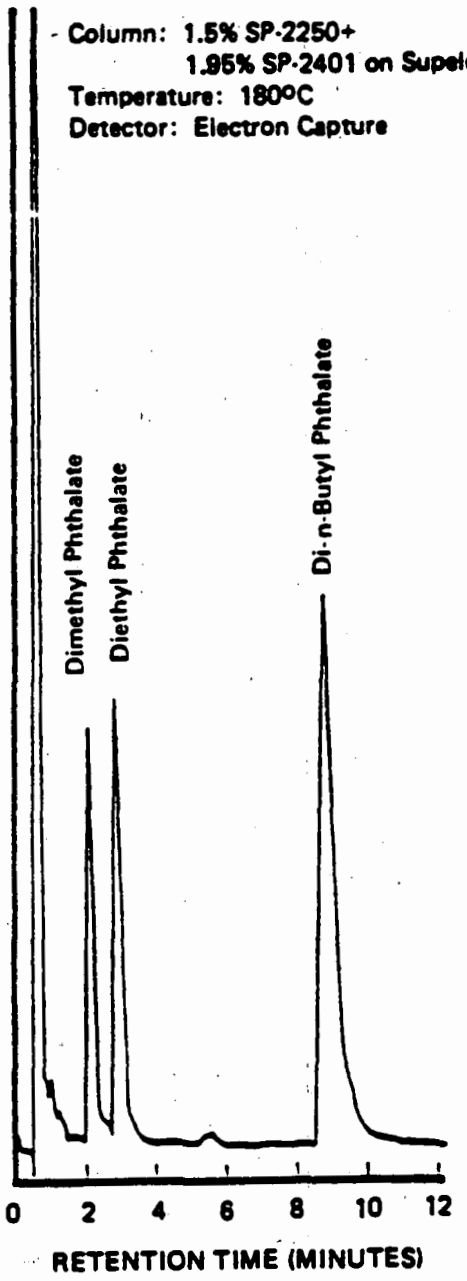


Figure 1. Gas chromatogram of phthalates (example 1).

Column: 1.5% SP-2250+
1.95% SP-2401 on Supelcoport
Temperature: 180°C
Detector: Electron Capture

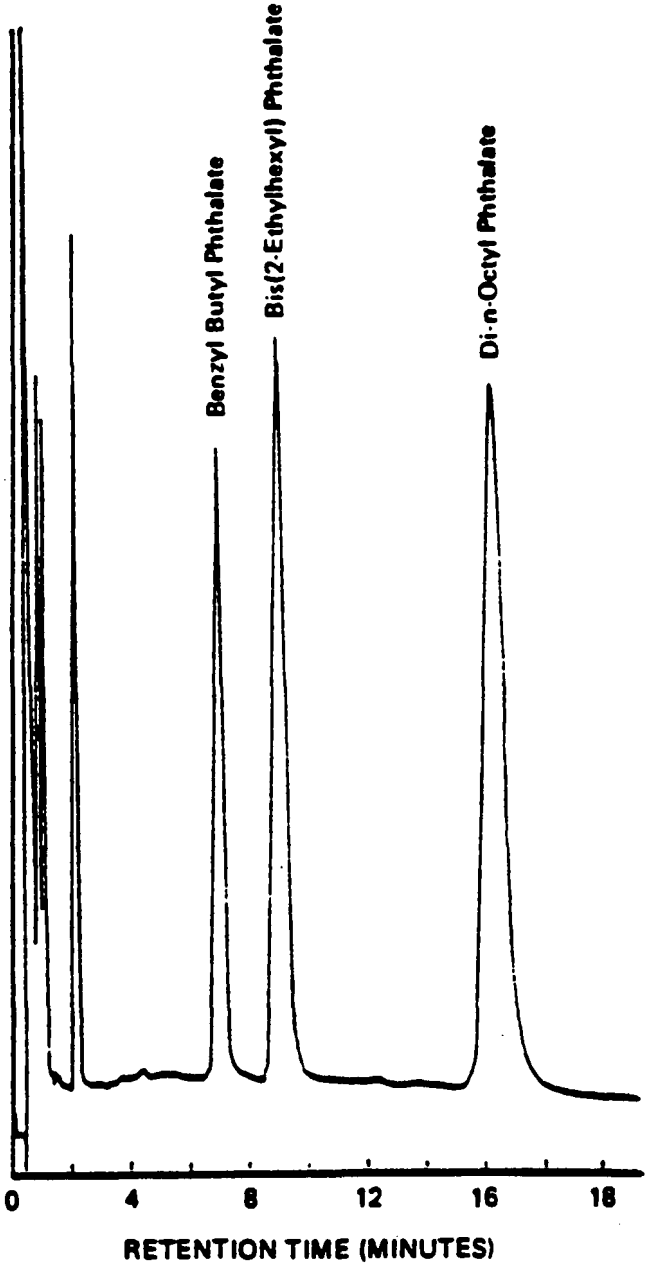


Figure 2. Gas chromatogram of phthalates (example 2).

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 The method was tested by 16 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 0.7 to 106 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

1. Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 1 - Phthalates. Report for EPA Contract 68-03-2606 (in preparation).

2. "Determination of Phthalates in Industrial and Municipal Wastewaters," EPA-600/4-81-063, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, October 1981.

3. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

4. "EPA Method Validation Study 16, Method 606 (Phthalate Esters)," Report for EPA Contract 68-03-2606 (in preparation).

5. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

6. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

TABLE 3. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_s (%)
Bis(2-ethylhexyl)phthalate	50	38.4	1.2-55.9	D-158
Butyl benzyl phthalate	10	4.2	5.7-11.0	30-136
Di-n-butyl phthalate	25	8.9	10.3-29.6	23-136
Diethyl phthalate	25	9.0	1.9-33.4	D-149
Dimethyl phthalate	25	9.5	1.3-35.5	D-156
Di-n-octyl phthalate	50	13.4	D-50.0	D-114

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 606. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

TABLE 4. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Bis(2-ethylhexyl) phthalate	0.53C+2.02	0.80$\bar{X}$-2.56	0.73$\bar{X}$-0.17
Butyl benzyl phthalate	0.82C+0.13	0.26$\bar{X}$+0.04	0.25$\bar{X}$+0.07
Di-n-butyl phthalate	0.79C+0.17	0.23$\bar{X}$+0.20	0.29$\bar{X}$+0.06
Diethyl phthalate	0.70C+0.13	0.27$\bar{X}$+0.05	0.45$\bar{X}$+0.11
Dimethyl phthalate	0.73C+0.17	0.26$\bar{X}$+0.14	0.44$\bar{X}$+0.31
Di-n-octyl phthalate	0.35C-0.71	0.38$\bar{X}$+0.71	0.62$\bar{X}$+0.34

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

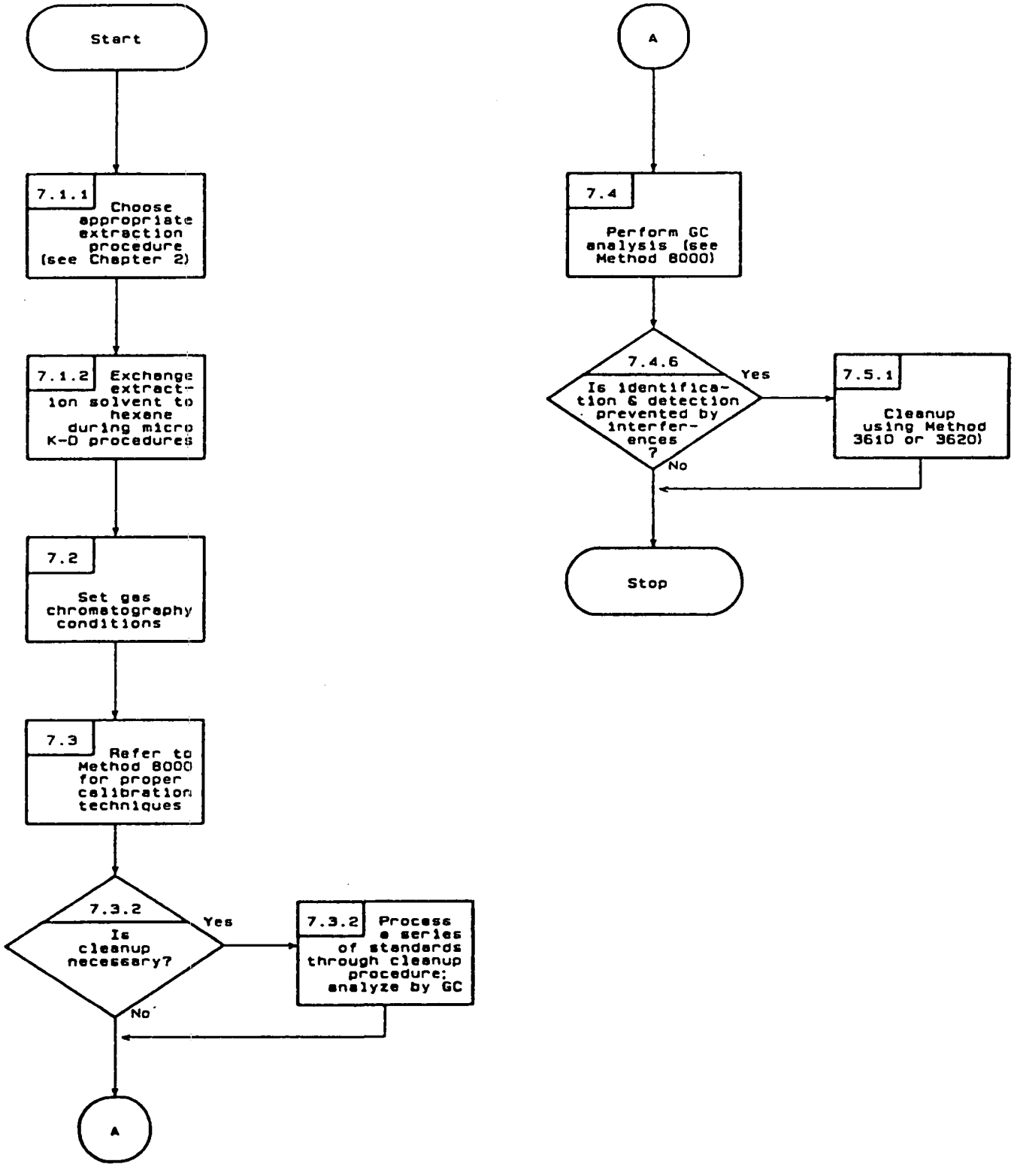
s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.

[a]Criteria from 40 CFR Part 136 for Method 606.


Start
7.1.1 Choose appropriate extraction procedure (see Chapter 2)
7.1.2 Exchange extraction solvent to hexane during micro K-D procedures
7.2 Set gas chromatography conditions
7.3 Refer to Method 8000 for proper calibration techniques
7.3.2 Is cleanup necessary?
Yes
7.3.2 Process a series of standards through cleanup procedure; analyze by GC
No
A
A
7.4 Perform GC analysis (see Method 8000)
7.4.6 Is identification & detection prevented by interferences ?
Yes
7.5.1 Cleanup using Method 3610 or 3620)
No
Stop

METHOD 8080

ORGANOCHLORINE PESTICIDES AND PCBs

1.0 SCOPE AND APPLICATION

1.1 Method 8080 is used to determine the concentration of various organochlorine pesticides and polychlorinated biphenyls (PCBs). Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8080 provides gas chromatographic conditions for the detection of ppb levels of certain organochlorine pesticides and PCBs. Prior to the use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL sample is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or a halogen-specific detector (HSD).

2.2 The sensitivity of Method 8080 usually depends on the level of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, Method 8080 may also be performed on samples that have undergone cleanup. Method 3620, Florisil Column Cleanup, by itself or followed by Method 3660, Sulfur Cleanup, may be used to eliminate interferences in the analysis.

3.0 INTERFERENCES

3.1 Refer to Methods 3500 (Section 3.5, in particular), 3600, and 8000.

3.2 Interferences by phthalate esters can pose a major problem in pesticide determinations when using the electron capture detector. These compounds generally appear in the chromatogram as large late-eluting peaks, especially in the 15% and 50% fractions from the Florisil cleanup. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination. The contamination from phthalate esters can be completely eliminated with a microcoulometric or electrolytic conductivity detector.

TABLE 1. GAS CHROMATOGRAPHY OF PESTICIDES AND PCBs[a]

Compound	Retention time (min) Col. 1	Retention time (min) Col. 2	Method Detection limit (ug/L)
Aldrin	2.40	4.10	0.004
α-BHC	1.35	1.82	0.003
β-BHC	1.90	1.97	0.006
δ-BHC	2.15	2.20	0.009
γ-BHC (Lindane)	1.70	2.13	0.004
Chlordane (technical)	e	e	0.014
4,4'-DDD	7.83	9.08	0.011
4,4'-DDE	5.13	7.15	0.004
4,4'-DDT	9.40	11.75	0.012
Dieldrin	5.45	7.23	0.002
Endosulfan I	4.50	6.20	0.014
Endosulfan II	8.00	8.28	0.004
Endosulfan sulfate	14.22	10.70	0.066
Endrin	6.55	8.10	0.006
Endrin aldehyde	11.82	9.30	0.023
Heptachlor	2.00	3.35	0.003
Heptachlor epoxide	3.50	5.00	0.083
Methoxychlor	18.20	26.60	0.176
Toxaphene	e	e	0.24
PCB-1016	e	e	nd
PCB-1221	e	e	nd
PCB-1232	e	e	nd
PCB-1242	e	e	0.065
PCB-1248	e	e	nd
PCB-1254	e	e	nd
PCB-1260	e	e	nd

[a]U.S. EPA. Method 617. Organochloride Pesticides and PCBs. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

e = Multiple peak response.

nd = not determined.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph:

4.1.1 **Gas Chromatograph:** Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 **Columns:**

4.1.2.1 Column 1: Supelcoport (100/120 mesh) coated with 1.5% SP-2250/1.95% SP-2401 packed in a 1.8-m x 4-mm I.D. glass column or equivalent.

4.1.2.2 Column 2: Supelcoport (100/120 mesh) coated with 3% OV-1 in a 1.8-m x 4-mm I.D. glass column or equivalent.

4.1.3 **Detectors:** Electron capture (ECD) or halogen specific (HSD) (i.e., electrolytic conductivity detector).

4.2 Kuderna-Danish (K-D) apparatus:

4.2.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts

4.2.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.2.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.4 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.5 Volumetric flasks: 10-, 50-, and 100-mL, ground-glass stopper.

4.6 Microsyringe: 10-uL.

4.7 Syringe: 5-mL.

4.8 Vials: Glass, 2-, 10-, and 20-mL capacity with Teflon-lined screw cap.

5.0 REAGENTS

5.1 Solvents: Hexane, acetone, toluene, isooctane (2,2,4-trimethylpentane) (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in isooctane and diluting to volume in a 10-mL volumetric flask. A small volume of toluene may be necessary to put some pesticides in solution. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels for each parameter of interest are prepared through dilution of the stock standards with isooctane. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

5.4 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with pesticide surrogates. Because GC/ECD data are much more subject to interference than GC/MS, a secondary surrogate is to be used when sample interference is apparent. Dibutylchlorendate (DBC) is also subject to acid and base degradation. Therefore, two surrogate standards are added to each sample; however, only one need be calculated for recovery. DBC is the primary surrogate and should be used whenever possible. However, if DBC recovery is low or compounds interfere with DBC, then the 2,4,5,6-tetrachloro-meta-xylene should be evaluated for acceptance. Proceed with corrective action when both surrogates are out of limits for a sample (Section 8.3). Method 3500, Section 5.3.2, indicates the proper procedure for preparing these surrogates.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.2.2 Increase the temperature of the hot water bath to about 90°C. Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.2.3 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C, if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with gas chromatographic analysis if further cleanup is not required.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1:** Set 5% methane/95% argon carrier gas flow at 60 mL/min flow rate. Column temperature is set at 200°C isothermal. When analyzing for the low molecular weight PCBs (PCB 1221-PCB 1248), it is advisable to set the oven temperature to 160°C.

7.2.2 **Column 2:** Set 5% methane/95% argon carrier gas flow at 60 mL/min flow rate. Column temperature held isothermal at 200°C. When analyzing for the low molecular weight PCBs (PCB 1221-PCB 1248), it is advisable to set the oven temperature to 140°C.

7.2.3 When analyzing for most or all of the analytes in this method, adjust the oven temperature and column gas flow so that 4,4'-DDT has a retention time of approximately 12 min.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day. Therefore, the GC column should be primed or deactivated by injecting a PCB or pesticide standard mixture approximately 20 times more concentrated than the mid-level standard. Inject this prior to beginning initial or daily calibration.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Examples of GC/ECD chromatograms for various pesticides and PCBs are shown in Figures 1 through 5.

7.4.4 Prime the column as per Paragraph 7.3.2.

7.4.5 DDT and endrin are easily degraded in the injection port if the injection port or front of the column is dirty. This is the result of buildup of high boiling residue from sample injection. Check for degradation problems by injecting a mid-level standard containing only 4,4'-DDT and endrin. Look for the degradation products of 4,4'-DDT (4,4'-DDE and 4,4'-DDD) and endrin (endrin ketone and endrin aldehyde). If degradation of either DDT or endrin exceeds 20%, take corrective action before proceeding with calibration, by following the GC system maintenance outlined in Section 7.7 of Method 8000. Calculate percent breakdown as follows:

$$\% \text{ breakdown for 4,4'-DDT} = \frac{\text{Total DDT degradation peak area (DDE + DDD)}}{\text{Total DDT peak area (DDT + DDE + DDD)}} \times 100$$

$$\% \text{ breakdown for Endrin} = \frac{\text{Total endrin degradation peak area (endrin aldehyde + endrin ketone)}}{\text{Total endrin peak area (endrin + endrin aldehyde + endrin ketone)}} \times 100$$

7.4.6 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.7 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.4.8 If peak detection and identification are prevented due to interferences, the hexane extract may need to undergo cleanup using Method 3620. The resultant extract(s) may be analyzed by GC directly or may undergo further cleanup to remove Sulfur using Method 3660.

7.5 Cleanup:

7.5.1 Proceed with Method 3620, followed by, if necessary, Method 3660, using the 10-mL hexane extracts obtained from Paragraph 7.1.2.3.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

7.6 Calculations (exerpted from U.S. FDA, PAM):

7.6.1 **Calculation of Certain Residues:** Residues which are mixtures of two or more components present problems in measurement. When they are found together, e.g., toxaphene and DDT, the problem of quantitation becomes even more difficult. In the following sections suggestions are offered for handling toxaphene, chlordane, PCB, DDT, and BHC. A column 10% DC-200 stationary phase was used to obtain the chromatograms in Figures 6-9.

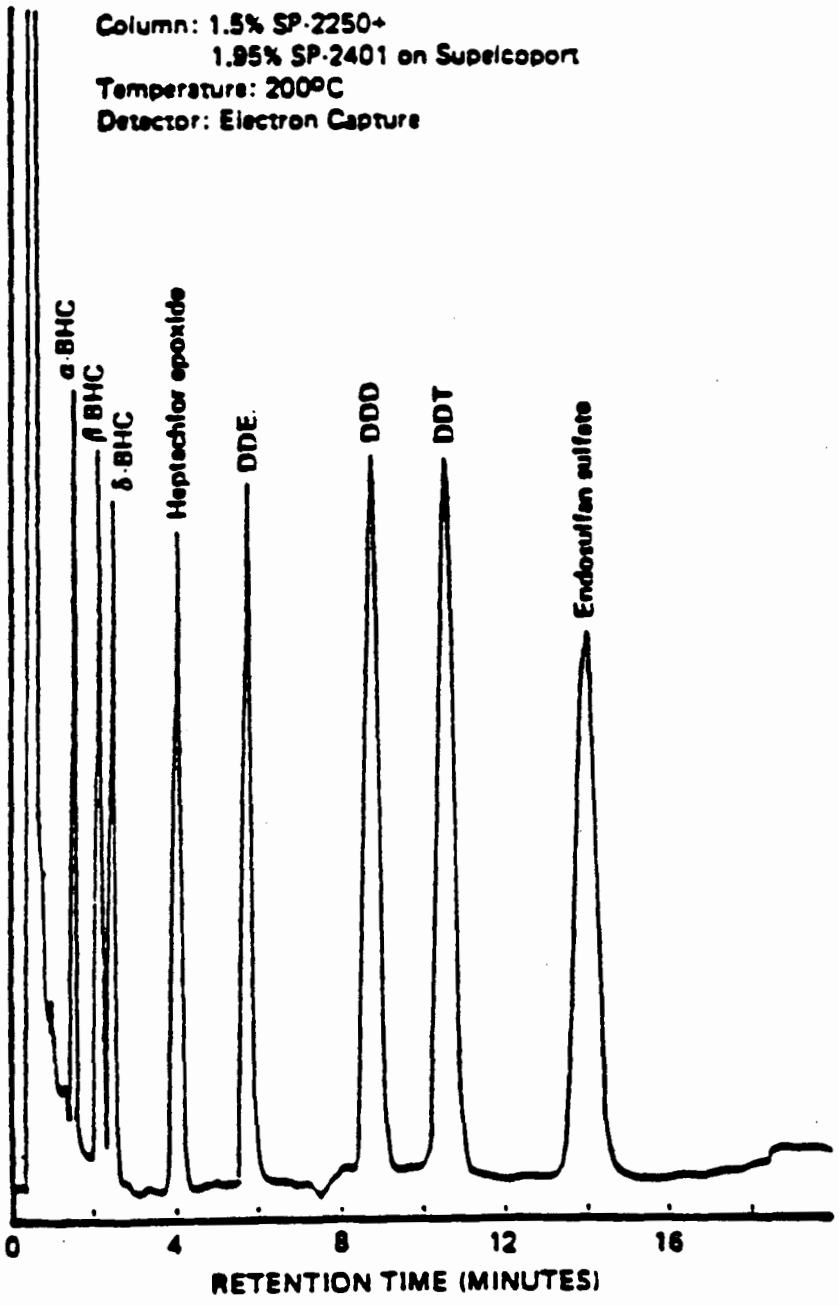


Figure 1. Gas chromatogram of pesticides.

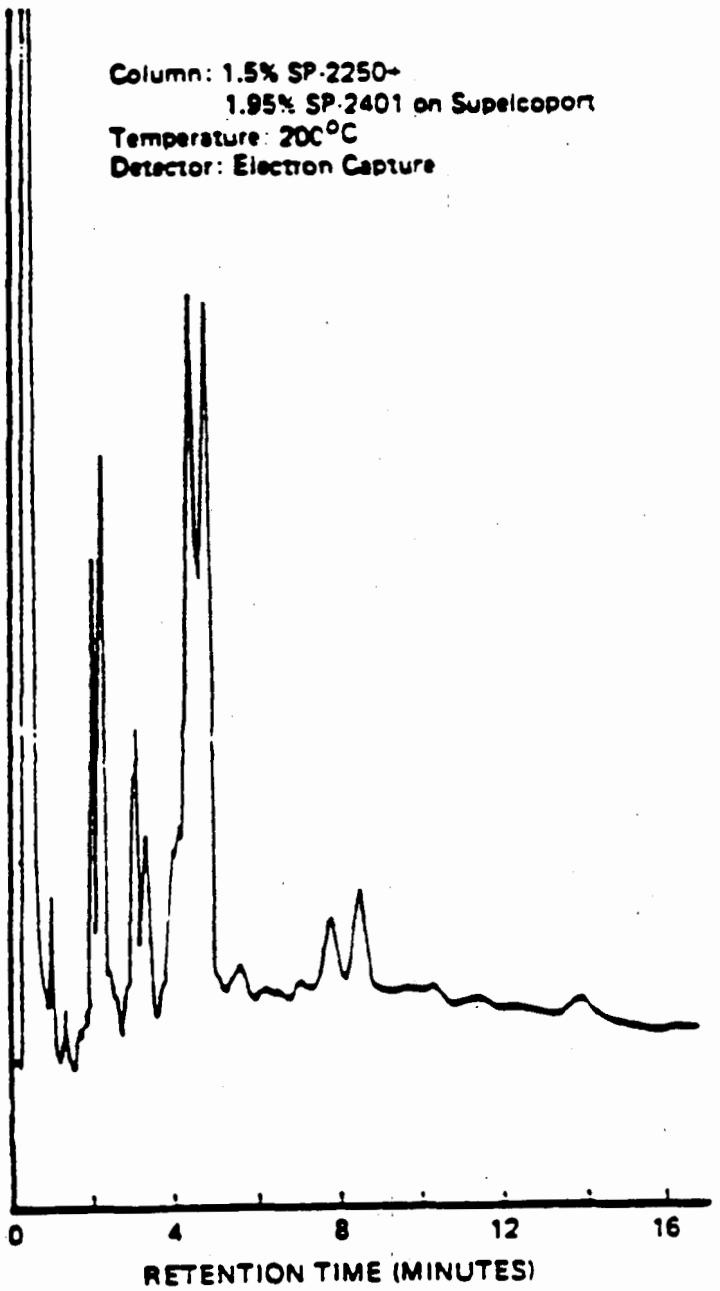


Figure 2. Gas chromatogram of chlordane.

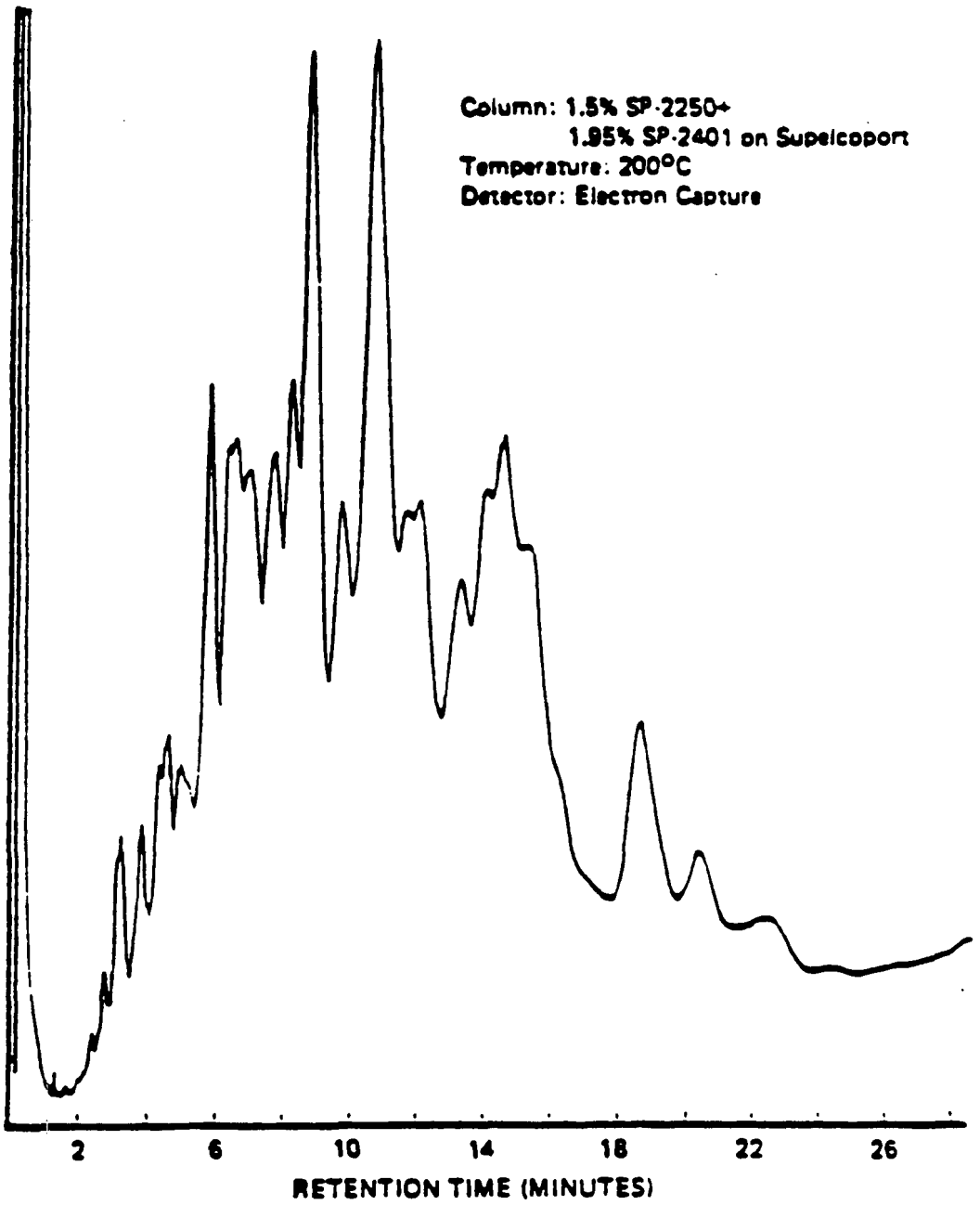


Figure 3. Gas chromatogram of toxaphene.

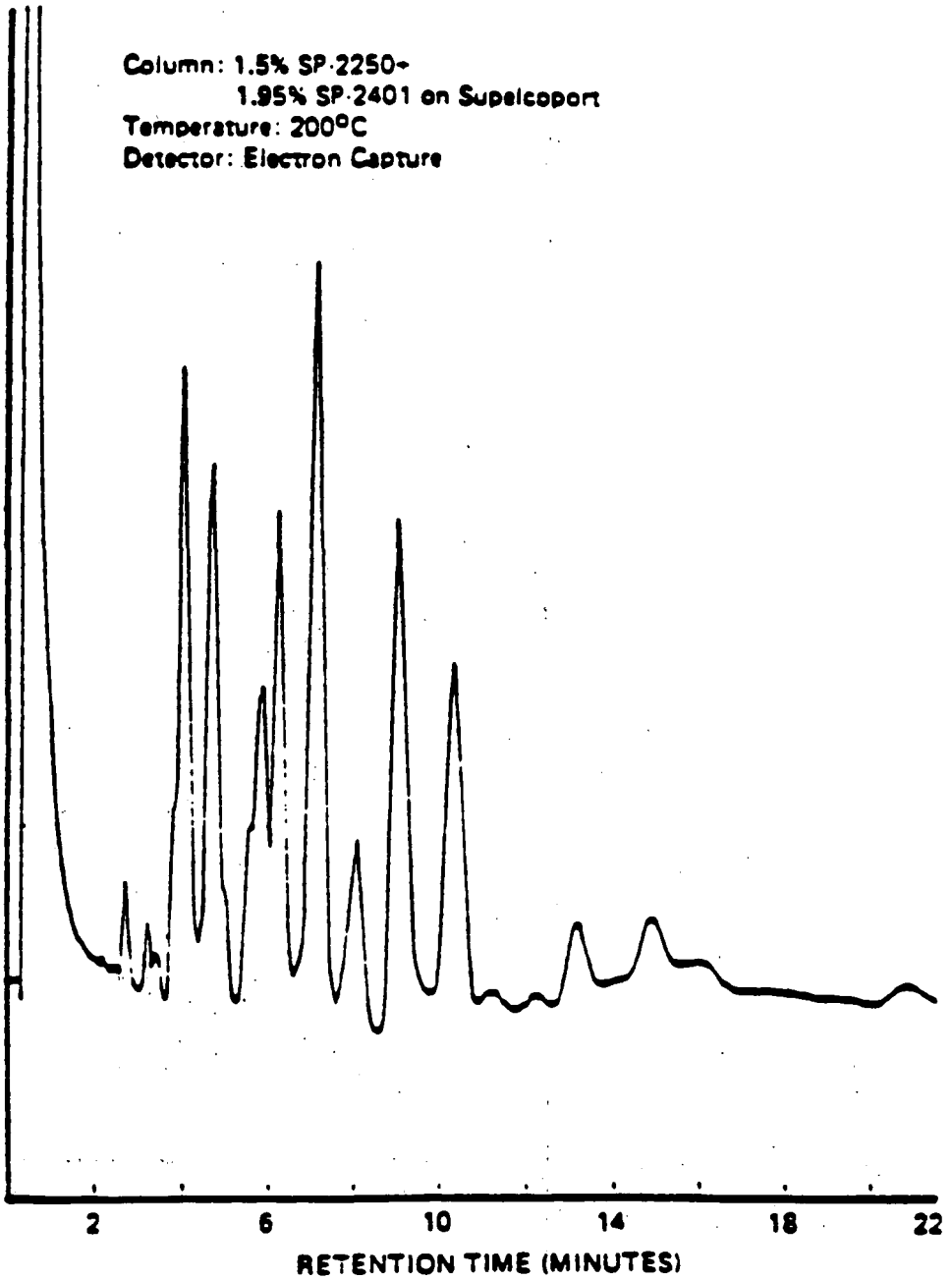


Figure 4. Gas chromatogram of PCB-1254.

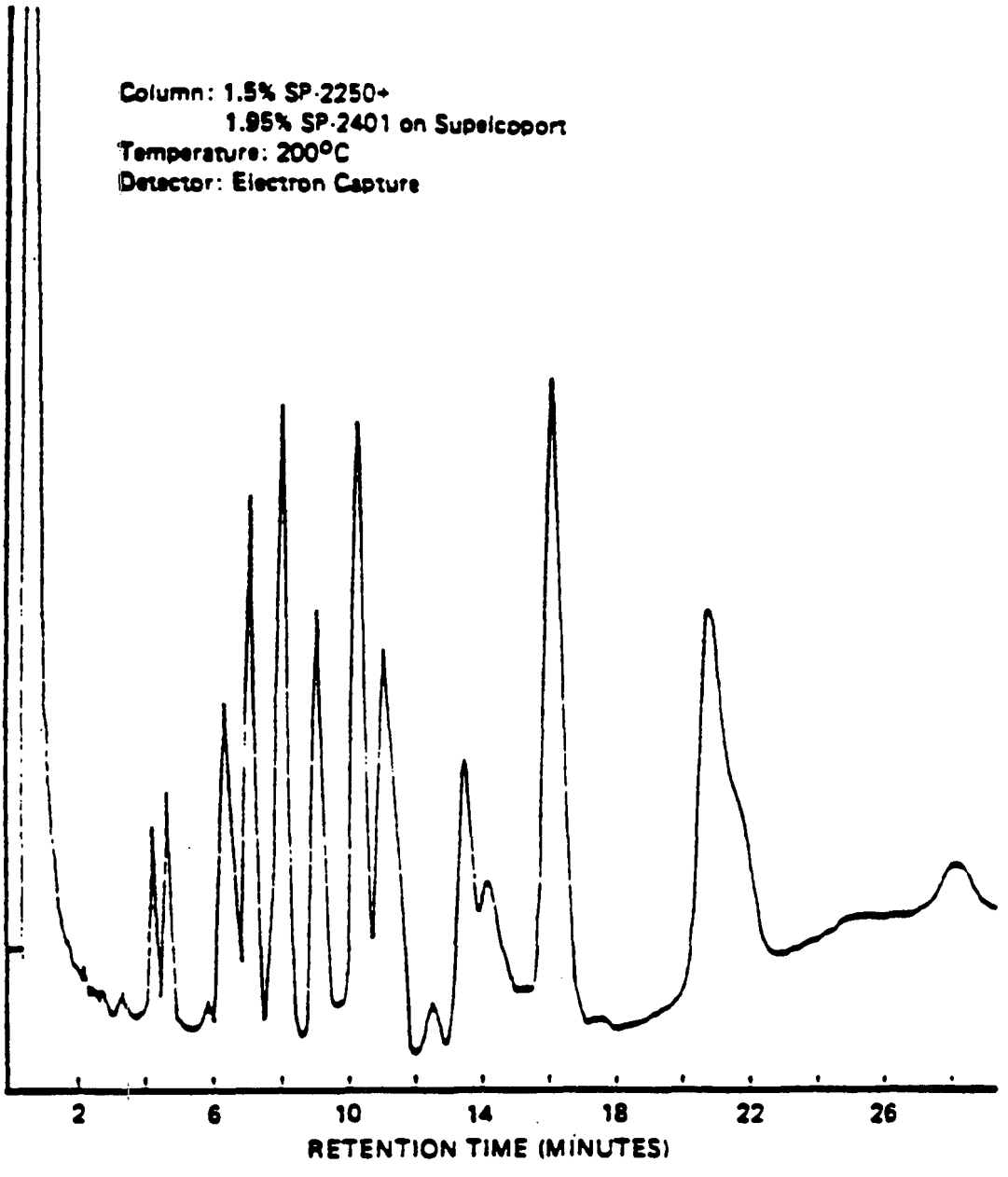


Figure 5. Gas chromatogram of PCB-1260.

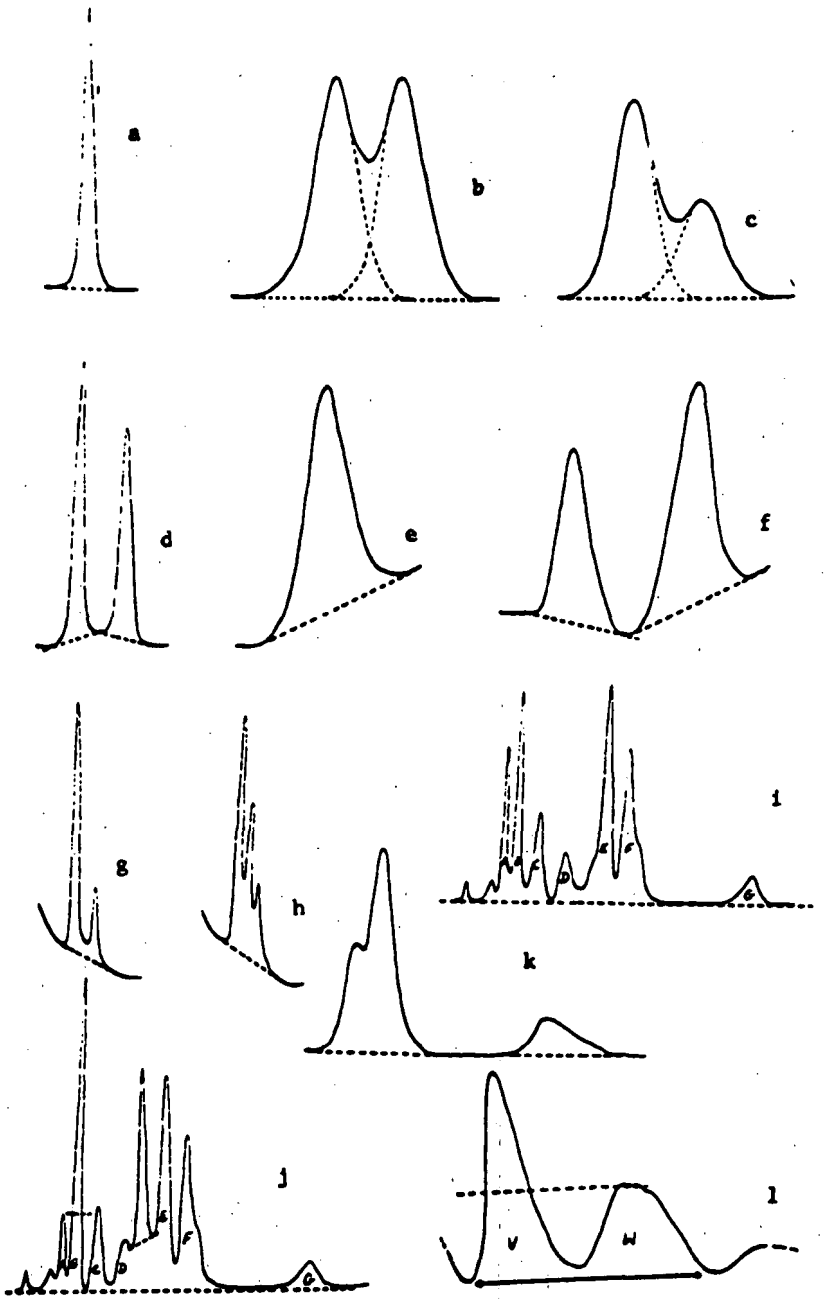


Fig. 6--Baseline construction for some typical gas chromatographic peaks. a, symmetrical separated flat baseline; b and c, overlapping flat baseline; d, separated (pen does not return to baseline between peaks); e, separated sloping baseline; f, separated (pen goes below baseline between peaks); g, α- and γ-BHC sloping baseline; h, α-, β-, and γ-BHC sloping baseline; i, chlordane flat baseline; j, heptachlor and heptachlor epoxide superimposed on chlordane; k, chair-shaped peaks, unsymmetrical peak; l, p,p'-DDT superimposed on toxaphene.

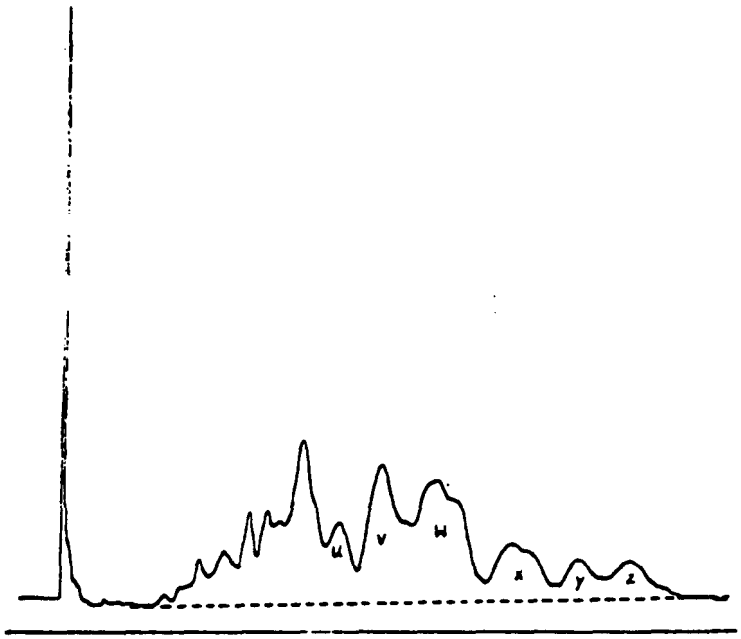


Fig. 7a--Baseline construction for multiple residues with standard toxaphene.

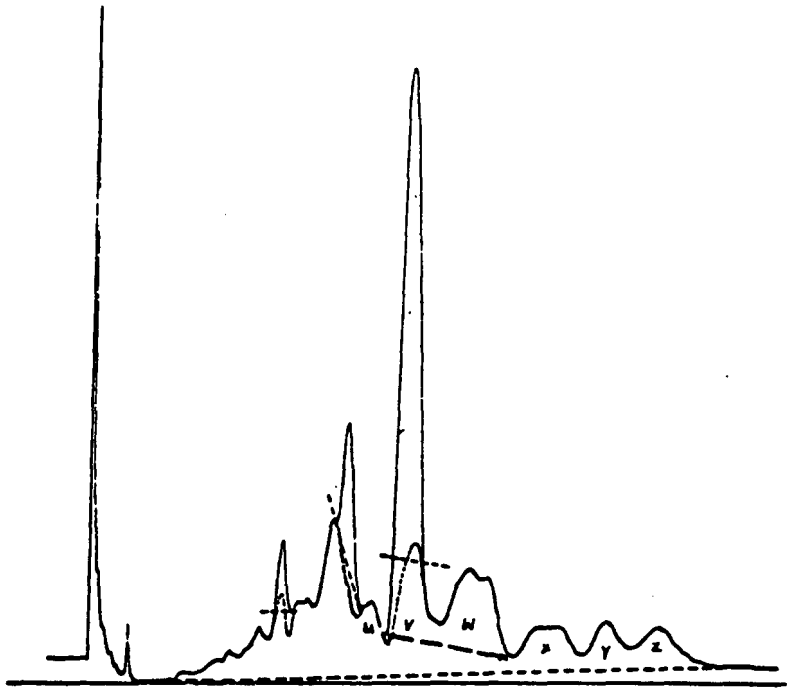


Fig. 7b--Baseline construction for multiple residues with toxaphene, DDE and o,p'-, and p,p'-DDT.

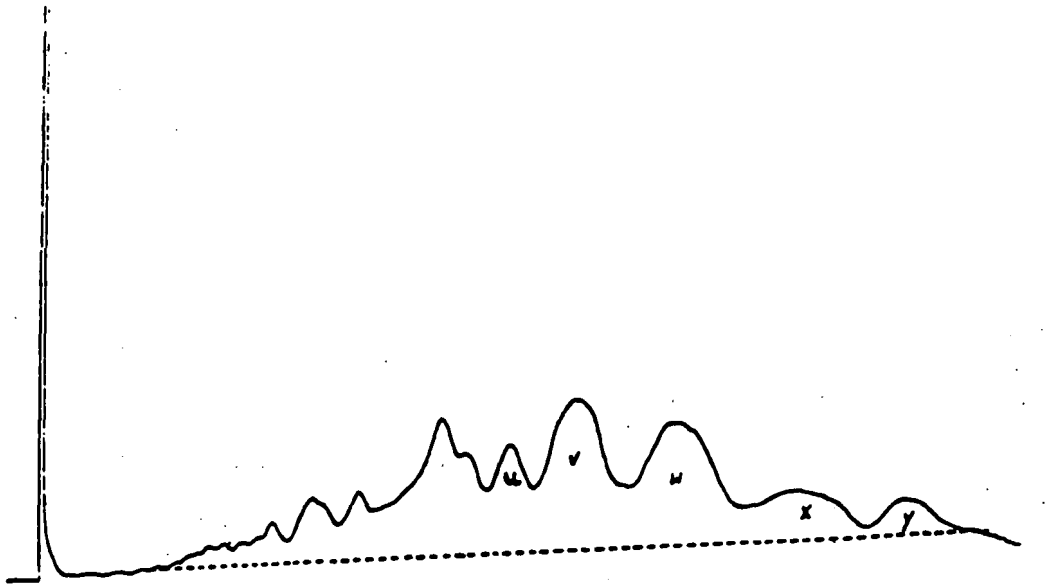


Fig. 8a--Baseline construction for multiple residues: standard toxaphene.

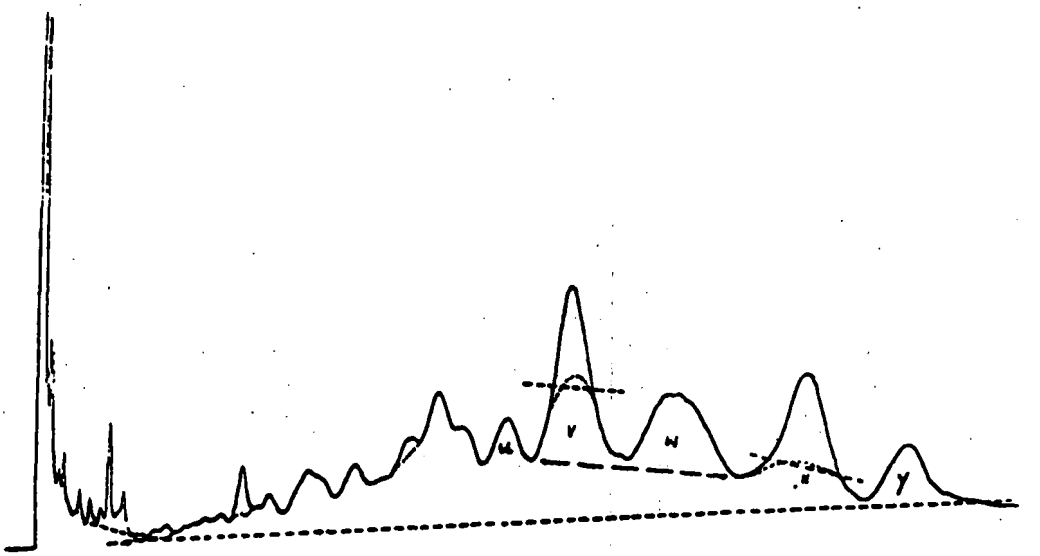


Fig. 8b--Baseline construction for multiple residues: rice bran with BHC, toxaphene, DDT, and methoxychlor.

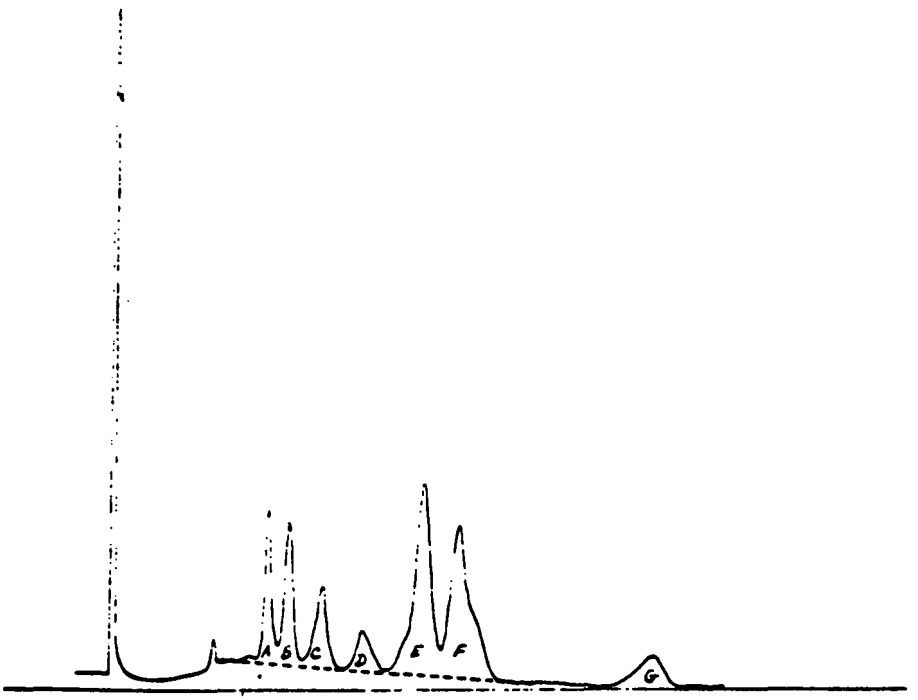


Fig. 9a--Baseline construction for multiple residues: standard chlordane.

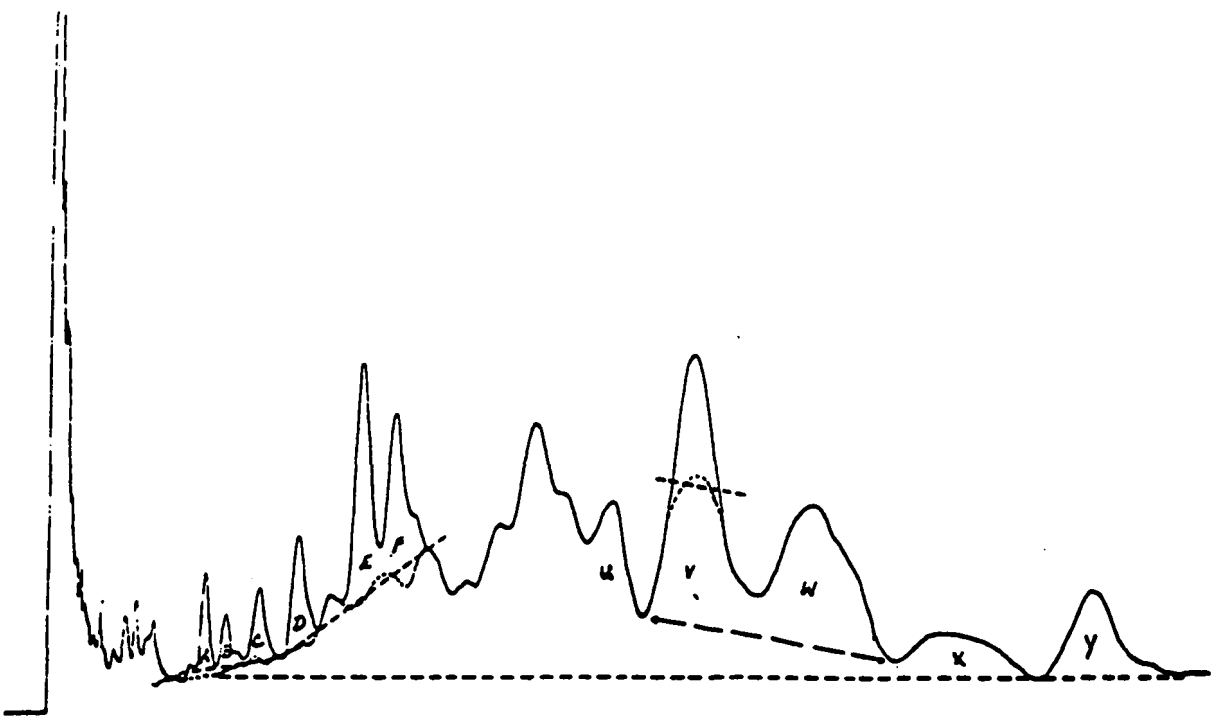


Fig. 9b—Baseline construction for multiple residues: rice bran with chlordane, toxaphene, and DDT.

7.6.2 **Toxaphene:** Quantitative calculation of toxaphene or Strobane is difficult, but reasonable accuracy can be obtained. To calculate toxaphene on GC/ECD: (a) adjust sample size so that toxaphene major peaks are 10-30% full-scale deflection (FSD); (b) inject a toxaphene standard that is estimated to be within ±10 ng of the sample; (c) construct the baseline of standard toxaphene between it extremities; and (d) construct the baseline under the sample, using the distances of the peak troughs to baseline on the standard as a guide (Figures 7, 8, and 9). This procedure is made difficult by the fact that the relative heights and widths of the peaks in the sample will probably not be identical to the standard. A toxaphene standard that has been passed through a Florisil column will show a shorter retention time for peak X and an enlargement of peak Y.

7.6.3 **Toxaphene and DDT:** If DDT is present, it will superimpose itself on toxaphene peak V. To determine the approximate baseline of the DDT, draw a line connecting the trough of peaks U and V with the trough of peaks W and X and construct another line parallel to this line which will just cut the top of peak W (Figure 61). This procedure was tested with ratios of standard toxaphene-DDT mixtures from 1:10 to 2:1 and the results of added and calculated DDT and toxaphene by the "parallel lines" method of baseline construction were within 10% of the actual values in all cases.

7.6.3.1 A series of toxaphene residues have been calculated using total peak area for comparison to the standard and also using area of the last four peaks only in both sample and standard. The agreement between the results obtained by the two methods justifies the use of the latter method for calculating toxaphene in a sample where the early eluting portion of the toxaphene chromatogram is interfered with by other substances.

7.6.3.2 The baseline for methoxychlor superimposed on toxaphene (Figure 8b) was constructed by overlaying the samples on a toxaphene standard of approximately the same concentration (Figure 8a) and viewing the charts against a lighted background.

7.6.4 Chlordane is a technical mixture of at least 11 major components and 30 or more minor ones. Gas chromatography-mass spectrometry and nuclear magnetic resonance analytical techniques have been applied to the elucidation of the chemical structures of the many chlordane constituents. Figure 9a is a chromatogram of standard chlordane. Peaks E and F are responses to trans- and cis-chlordane, respectively. These are the two major components of technical chlordane, but the exact percentage of each in the technical material is not completely defined and is not consistent from batch to batch. Other labelled peaks in Figure 9a are thought to represent: A, monochlorinated adduct of pentachlorocyclopentadiene with cyclopentadiene; B, coelution of heptachlor and α-chlordene; C, coelution of β-chlordene and γ-chlordene;

D, a chlordane analog; G, coelution of cis-nonachlor and "Compound K," a chlordane isomer. The right "shoulder" of peak F is caused by trans-nonachlor.

7.6.4.1 The GC pattern of a chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of chlordane can consist of almost any combination of: constituents from the technical chlordane; plant and/or animal metabolities; and products of degradation caused by exposure to environmental factors such as water and sunlight. Only limited information is available on which residue GC patterns are likely to occur in which samples types, and even this information may not be applicable to a situation where the route of exposure is unusual. For example, fish exposed to a recent spill of technical chlordane will contain a residue drastically different from a fish whose chlordane residue was accumulated by ingestion of smaller fish or of vegetation, which in turn had accumulated residues because chlordane was in the water from agricultural runoff.

7.6.4.2 Because of this inability to predict a chlordane residue GC pattern, it is not possible to prescribe a single method for the quantitation of chlordane residues. The analyst must judge whether or not the residue's GC pattern is sufficiently similar to that of a technical chlordane reference material to use the latter as a reference standard for quantitation.

7.6.4.3 When the chlordane residue does <u>not</u> resemble technical chlordane, but instead consists primarily of individual, identifiable peaks, quantitate each peak separately against the appropriate reference materials and report the individual residues. (Reference materials are available for at least 11 chlordane constituents, metabolites or degradation products which may occur in the residue.)

7.6.4.4 When the GC pattern of the residue resembles that of technical chlordane, quantitate chlordane residues by comparing the total area of the chlordane chromatogram from peaks A through F (Figure 9a) in the sample versus the same part of the standard chromatogram. Peak G may be obscured in a sample by the presence of other pesticides. If G is not obscured, include it in the measurement for both standard and sample. If the heptachlor epoxide peak is relatively small, include it as part of the total chlordane area for calculation of the residue. If heptachlor and/or heptachlor epoxide are much out of proportion as in Figure 6j, calculate these separately and subtract their areas from total area to give a corrected chlordane area. (Note that octachlor epoxide, metabolite of chlordane, can easily be mistaken for heptachlor epoxide on a nonpolar GC column.)

7.6.4.5 To measure the total area of the chlordane chromatogram, proceed as in Section 7.6.2 on toxaphene. Inject an amount of technical chlordane standard which will produce a chromatogram in which peaks E and F are approximately the same size as those in the sample chromatograms. Construct the baseline beneath the standard from the beginning of peak A to the end of peak F as shown in Figure 9a. Use the distance from the trough between peaks E and F to the baseline in the chromatogram of the standard to construct the baseline in the chromatogram of the sample. Figure 9b shows how the presence of toxaphene causes the baseline under chlordane to take an upward angle. When the size of peaks E and F in standard and sample chromatograms are the same, the distance from the trough of the peaks to the baselines should be the same. Measurement of chlordane area should be done by total peak area if possible.

NOTE: A comparison has been made of the total peak area integration method and the addition of peak heights method for several samples containing chlordane. The peak heights A, B, C, D, E, and F were measured in millimeters from peak maximum of each to the baseline constructed under the total chlordane area and were then added together. These results obtained by the two techniques are too close to ignore this method of "peak height addition" as a means of calculating chlordane. The technique has inherent difficulties because not all the peaks are symmetrical and not all are present in the same ratio in standard and in sample. This method does offer a means of calculating results if no means of measuring total area is practical.

7.6.5 **Polychlorinated biphenyls (PCBs):** Quantitation of residues of PCB involves problems similar to those encountered in the quantitation of toxaphene, Strobane, and chlordane: in each case, the chemical is made up of numerous compounds and so the chromatograms are multi-peak; also in each case the chromatogram of the residue may not match that of the standard.

7.6.5.1 Mixtures of PCB of various chlorine contents were sold for many years in the U.S. by the Monsanto Co. under the tradename Aroclor (1200 series and 1016). Though these Aroclors are no longer marketed, the PCBs remain in the environment and are sometime found as residues in foods, especially fish.

7.6.5.2 PCB residues are quantitated by comparison to one or more of the Aroclor materials, depending on the chromatographic pattern of the residue. A choice must be made as to which Aroclor or mixture of Aroclors will produce a chromatogram most similar to that of the residue. This may also involve a judgment about what proportion of the different Aroclors to combine to produce the appropriate reference material.

7.6.5.3 Quantitate PCB residues by comparing total area or height of residue peaks to total area of height of peaks from appropriate Aroclor(s) reference materials. Measure total area or height response from common baseline under all peaks. Use only those peaks from sample that can be attributed to chlorobiphenyls. These peaks must also be present in chromatogram of reference materials. Mixture of Aroclors may be required to provide best match of GC patterns of sample and reference.

7.6.6 **DDT:** DDT found in samples often consists of both o,p'- and p,p'-DDT. Residues of DDE and TDE are also frequently present. Each isomer of DDT and its metabolites should be quantitated using the pure standard of that compound and reported as such.

7.6.7 **Hexachlorocyclohexane (BHC, from the former name, benzene hexachloride):** Technical grade BHC is a cream-colored amorphous solid with a very characteristic musty odor; it consists of a mixture of six chemically distinct isomers and one or more heptachloro-cyclohexanes and octachloro-cyclohexanes.

7.6.7.1 Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. The elimination rate of the isomers fed to rats was 3 weeks for the α-, γ-, and δ-isomers and 14 weeks for the β-isomer. Thus it may be possible to have any combination of the various isomers in different food commodities. BHC found in dairy products usually has a large percentage of β-isomer.

7.6.7.2 Individual isomers (α, β, γ, and δ) were injected into gas chromatographs equipped with flame ionization, microcoulometric, and electron capture detectors. Response for the four isomers is very nearly the same whether flame ionization or microcoulometric GLC is used. The α-, γ-, and δ-isomers show equal electron affinity. β-BHC shows a much weaker electron affinity compared to the others isomers.

7.6.7.3 Quantitate each isomer (α, β, γ, and δ) separately against a standard of the respective pure isomer, using a GC column which separates all the isomers from one another.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Mandatory quality control to evaluate the GC system operation is found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each single-component parameter of interest at the following concentrations in acetone: 4,4'-DDD, 10 ug/mL; 4,4'-DDT, 10 ug/mL; endosulfan II, 10 ug/mL; endosulfan sulfate, 10 ug/mL; endrin, 10ug/mL; and any other single-component pesticide, 2 ug/mL. If this method is only to be used to analyze for PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multi-component parameter at a concentration of 50 ug/mL in acetone.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.4 GC/MS confirmation: Any compounds confirmed by two columns may also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS as determined by the laboratory generated detection limits.

8.4.1 The GC/MS would normally require a minimum concentration of 10 ng/uL in the final extract, for each single-component compound.

8.4.2 The pesticide extract and associated blank should be analyzed by GC/MS as per Section 7.0 of Method 8270.

8.4.3 The confirmation may be from the GC/MS analysis of the base/neutral-acid extractables extracts (sample and blank). However, if the compounds are not detected in the base/neutral-acid extract even though the concentration is high enough, a GC/MS analysis of the pesticide extract should be performed.

8.4.4 A reference standard of the compound must also be analyzed by GC/MS. The concentration of the reference standard must be at a level that would demonstrate the ability to confirm the pesticides/PCBs identified by GC/ECD.

9.0 METHOD PERFORMANCE

9.1 The method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations. Concentrations used in the study ranged from 0.5 to 30 ug/L for single-component pesticides and from 8.5 to 400 ug/L for multi-component parameters. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, optional cleanup techniques, and calibration procedures used.

10.0 REFERENCES

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12. Sawyer, L.D., JAOAC, 56, 1015-1023 (1973), 61 272-281 (1978), 61 282-291 (1978).

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TABLE 3. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_S (%)
Aldrin	2.0	0.42	1.08-2.24	42-122
α-BHC	2.0	0.48	.98-2.44	37-134
β-BHC	2.0	0.64	0.78-2.60	17-147
δ-BHC	2.0	0.72	1.01-2.37	19-140
γ-BHC	2.0	0.46	0.86-2.32	32-127
Chlordane	50	10.0	27.6-54.3	45-119
4,4'-DDD	10	2.8	4.8-12.6	31-141
4,4'-DDE	2.0	0.55	1.08-2.60	30-145
4,4'-DDT	10	3.6	4.6-13.7	25-160
Dieldrin	2.0	0.76	1.15-2.49	36-146
Endosulfan I	2.0	0.49	1.14-2.82	45-153
Endosulfan II	10	6.1	2.2-17.1	D-202
Endosulfan Sulfate	10	2.7	3.8-13.2	26-144
Endrin	10	3.7	5.1-12.6	30-147
Heptachlor	2.0	0.40	0.86-2.00	34-111
Heptachlor epoxide	2.0	0.41	1.13-2.63	37-142
Toxaphene	50	12.7	27.8-55.6	41-126
PCB-1016	50	10.0	30.5-51.5	50-114
PCB-1221	50	24.4	22.1-75.2	15-178
PCB-1232	50	17.9	14.0-98.5	10-215
PCB-1242	50	12.2	24.8-69.6	39-150
PCB-1248	50	15.9	29.0-70.2	38-158
PCB-1254	50	13.8	22.2-57.9	29-131
PCB-1260	50	10.4	18.7-54.9	8-127

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_S = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 608. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

TABLE 4. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Aldrin	0.81C+0.04	0.16$\bar{X}$-0.04	0.20$\bar{X}$-0.01
α-BHC	0.84C+0.03	0.13$\bar{X}$+0.04	0.23$\bar{X}$-0.00
β-BHC	0.81C+0.07	0.22$\bar{X}$+0.02	0.33$\bar{X}$-0.95
δ-BHC	0.81C+0.07	0.18$\bar{X}$+0.09	0.25$\bar{X}$+0.03
γ-BHC	0.82C-0.05	0.12$\bar{X}$+0.06	0.22$\bar{X}$+0.04
Chlordane	0.82C-0.04	0.13$\bar{X}$+0.13	0.18$\bar{X}$+0.18
4,4'-DDD	0.84C+0.30	0.20$\bar{X}$-0.18	0.27$\bar{X}$-0.14
4,4'-DDE	0.85C+0.14	0.13$\bar{X}$+0.06	0.28$\bar{X}$-0.09
4,4'-DDT	0.93C-0.13	0.17$\bar{X}$+0.39	0.31$\bar{X}$-0.21
Dieldrin	0.90C+0.02	0.12$\bar{X}$+0.19	0.16$\bar{X}$+0.16
Endosulfan I	0.97C+0.04	0.10$\bar{X}$+0.07	0.18$\bar{X}$+0.08
Endosulfan II	0.93C+0.34	0.41$\bar{X}$-0.65	0.47$\bar{X}$-0.20
Endosulfan Sulfate	0.89C-0.37	0.13$\bar{X}$+0.33	0.24$\bar{X}$+0.35
Endrin	0.89C-0.04	0.20$\bar{X}$+0.25	0.24$\bar{X}$+0.25
Heptachlor	0.69C+0.04	0.06$\bar{X}$+0.13	0.16$\bar{X}$+0.08
Heptachlor epoxide	0.89C+0.10	0.18$\bar{X}$-0.11	0.25$\bar{X}$-0.08
Toxaphene	0.80C+1.74	0.09$\bar{X}$+3.20	0.20$\bar{X}$+0.22
PCB-1016	0.81C+0.50	0.13$\bar{X}$+0.15	0.15$\bar{X}$+0.45
PCB-1221	0.96C+0.65	0.29$\bar{X}$-0.76	0.35$\bar{X}$-0.62
PCB-1232	0.91C+10.79	0.21$\bar{X}$-1.93	0.31$\bar{X}$+3.50
PCB-1242	0.93C+0.70	0.11$\bar{X}$+1.40	0.21$\bar{X}$+1.52
PCB-1248	0.97C+1.06	0.17$\bar{X}$+0.41	0.25$\bar{X}$-0.37
PCB-1254	0.76C+2.07	0.15$\bar{X}$+1.66	0.17$\bar{X}$+3.62
PCB-1260	0.66C+3.76	0.22$\bar{X}$-2.37	0.39$\bar{X}$-4.86

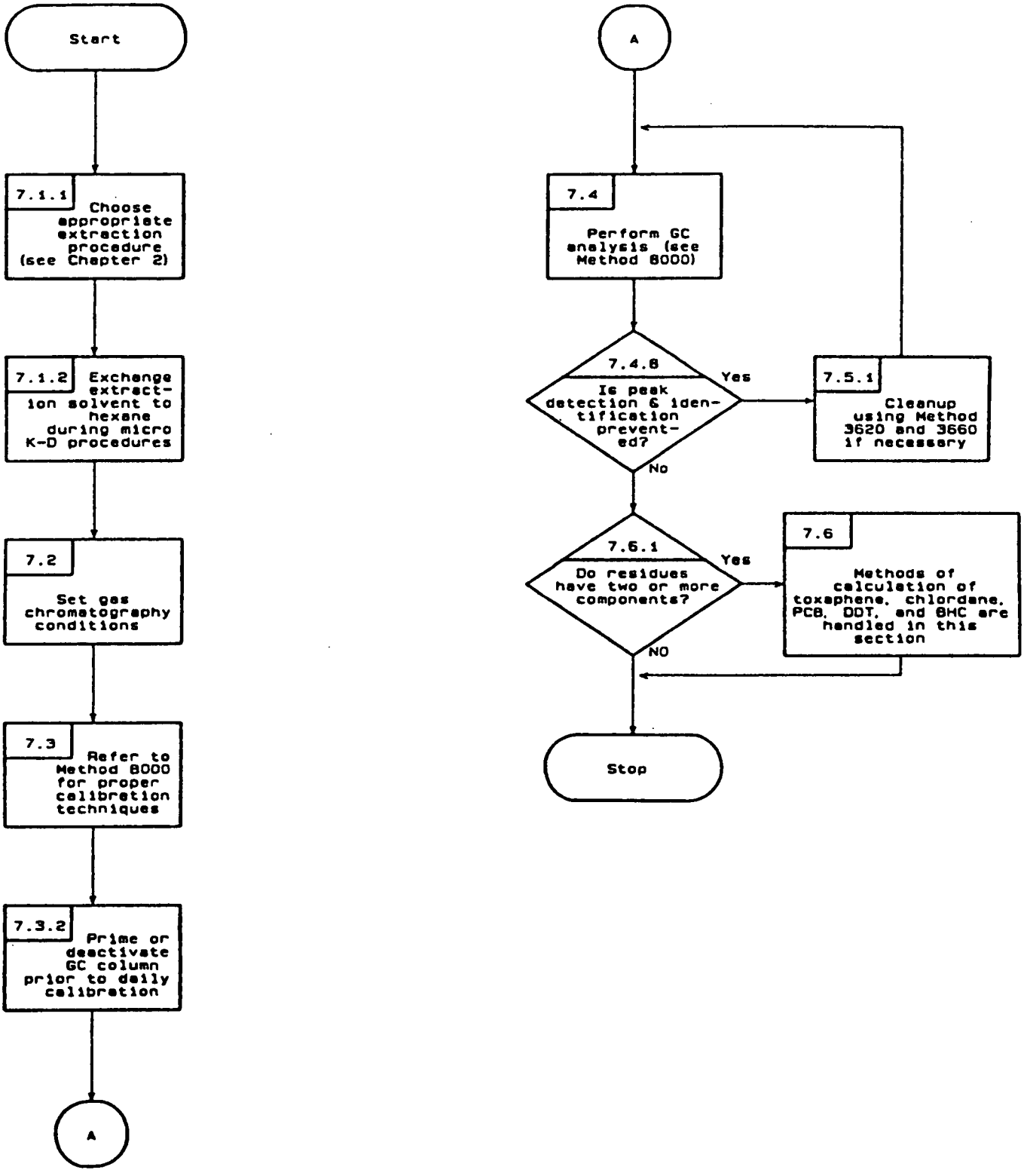
x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.


Start
7.1.1 Choose appropriate extraction procedure (see Chapter 2)
7.1.2 Exchange extraction solvent to hexane during micro K-D procedures
7.2 Set gas chromatography conditions
7.3 Refer to Method 8000 for proper calibration techniques
7.3.2 Prime or deactivate GC column prior to daily calibration
A
A
7.4 Perform GC analysis (see Method 8000)
7.4.8 Is peak detection & identification prevented?
Yes
7.5.1 Cleanup using Method 3620 and 3660 if necessary
No
7.6.1 Do residues have two or more components?
Yes
7.6 Methods of calculation of toxaphene, chlordane, PCB, DDT, and BHC are handled in this section
NO
Stop

METHOD 8090

NITROAROMATICS AND CYCLIC KETONES

1.0 SCOPE AND APPLICATION

1.1 Method 8090 is used to determine the concentration of various nitroaromatic and cyclic ketone compounds. Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8090 provides gas chromatographic conditions for the detection of ppb levels of nitroaromatic and cyclic ketone compounds. Prior to use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL aliquot of the extract is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or a flame ionization detector (FID). The dinitrotoluenes are determined using ECD, whereas the other compounds amenable to this method are determined using FID.

2.2 If interferences prevent proper detection of the analytes, the method may also be performed on extracts that have undergone cleanup.

3.0 INTERFERENCES

3.1 Refer to Method 3500, 3600, and 8000.

3.2 Solvents, reagents, glassware, and other sample-processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.3 Interferences coextracted from samples will vary considerably from source to source, depending upon the waste being sampled. Although general cleanup techniques are recommended as part of this method, unique samples may require additional cleanup.

TABLE 1. GAS CHROMATOGRAPHY OF NITROAROMATICS AND ISOPHORONE

Compound	Retention time (min)		Method detection limit (ug/L)	
	Col. 1[a]	Col. 2[b]	ECD	FID
Isophorone	4.49	5.72	15.7	5.7
Nitrobenzene	3.31	4.31	13.7	3.6
2,4-Dinitrotoluene	5.35	6.54	0.02	-
2,6-Dinitrotoluene	3.52	4.75	0.01	-
Dinitrobenzene				
Naphthoquinone				

[a]Column 1: Gas-Chrom Q (80/100 mesh) coated with 1.95% QF-1/1.5% OV-17 packed in a 1.2-m x 2-mm or 4-mm I.D. glass column. A 2-mm I.D. column and nitrogen gas at 44 mL/min flow rate were used when determining isophorone and nitrobenzene by GC/FID. The column temperature was held isothermal at 85°C. A 4-mm I.D. column and 10% methane/90% argon carrier gas at 44 mL/min flow rate were used when determining the dinitrotoluenes by GC/ECD. The column temperature was held isothermal at 145°C.

[b]Column 2: Gas-Chrom Q (80/100 mesh) coated with 3% OV-101 packed in a 3.0-m x 2-mm or 4-mm I.D. glass column. A 2-mm I.D. column and nitrogen carrier gas at 44 mL/min flow rate were used when determining isophorone and nitrobenzene by GC/FID. The column temperature was held isothermal at 100°C. A 4-mm I.D. column and 10% methane/90% argon carrier gas at 44 mL/min flow rate were used to determine the dinitrotoluenes by GC/ECD. The column temperature was held isothermal at 150°C.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]Multiply the Method Detection Limits in Table 1 by the Factor to determine the PQL for each analyte in the matrix to be analyzed.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph:

4.1.1 **Gas chromatograph:** Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.2 **Columns:**

4.1.2.1 Column 1: 1.2-m x 2- or 4-mm I.D. glass column packed with 1.95% QF-1/1.5% OV-17 on Gas-Chrom Q (80/100 mesh) or equivalent.

4.1.2.2 Column 2: 3.0-m x 2- or 4-mm I.D. glass column packed with 3% OV-101 on Gas-Chrom Q (80/100 mesh) or equivalent.

4.1.3 **Detectors:** Flame ionization (FID) or electron capture (ECD).

4.2 Kuderna-Danish (K-D) apparatus:

4.2.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts

4.2.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.2.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.4 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.5 Volumetric flasks: 10-, 50-, and 100-mL, ground-glass stopper.

4.6 Microsyringe: 10-uL.

4.7 Syringe: 5-mL.

4.8 Vials: Glass, 2-, 10-, and 20-mL capacity with Teflon-lined screw cap.

5.0 REAGENTS

5.1 Solvents: hexane, acetone (pesticide quality or equivalent.)

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in hexane and diluting to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels are prepared through dilution of the stock standards with hexane. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with a check standard indicates a problem.

5.4 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with hexane.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each

sample, standard, and reagent water blank with one or two surrogates (e.g., 2-fluorobiphenyl) recommended to encompass the range of the temperature program used in this method. Method 3500, Section 5.3.1.1, details instructions on the preparation of base/neutral surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a pH between 5 to 9 with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange may be performed in one of two ways, depending on the data requirements. If the detection limits cited in Table 1 must be achieved, the exchange should be performed as described starting in Section 7.1.4. If these detection limits are not necessary, solvent exchange is performed as outlined in Section 7.1.3.

7.1.3 **Solvent exchange when detection limits in Table 1 are not required:**

7.1.3.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.3.2 Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. The extract will be handled differently

at this point, depending on whether or not cleanup is needed. If cleanup is not required, proceed to Paragraph 7.1.3.3. If cleanup is needed, proceed to Paragraph 7.1.3.4.

7.1.3.3 If cleanup of the extract is not required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with gas chromatographic analysis.

7.1.3.4 If cleanup of the extract is required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with a minimum amount of hexane. A 5-mL syringe is recommended for this operation. Add a clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding about 0.5 mL of hexane to the top. Place the micro-K-D apparatus on the water bath (80°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.3.5 Remove the micro-Snyder column and rinse the flask and its lower joint into the concentrator tube with 0.2 mL of hexane. Adjust the extract volume to 2.0 mL and proceed with Method 3620.

7.1.4 **Solvent exchange when detection limits listed in Table 1 must be achieved:**

7.1.4.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.4.2 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of methylene chloride. A 5-mL syringe is recommended for this operation. Add 1-2 mL of hexane, a clean boiling chip, and attach a two-ball micro-Snyder column. Prewet the column by adding 0.5 mL of hexane to the top. Place the micro-K-D apparatus on the water bath (60-65°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.4.3 Remove the micro-Snyder column and rinse the flask and its lower joint into the concentrator tube with a minimum amount of hexane. The volume of the extract should be adjusted to 1.0 mL if the extract will be analyzed without cleanup. If the extract will require cleanup, adjust the volume to 2.0 mL with hexane. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with either gas chromatographic analysis or with cleanup, as necessary.

7.2 Gas chromatography conditions (Recommended): The determination of dinitrotoluenes should be performed using GC/ECD. All other compounds amenable to this method are to be analyzed by GC/FID.

7.2.1 **Column 1:** Set 10% methane/90% argon carrier gas flow at 44 mL/min flow rate. For a 2-mm I.D. column, set the temperature at 85°C isothermal. For a 4-mm I.D. column, set the temperature at 145°C isothermal.

7.2.2 **Column 2:** Set 10% methane/90% argon carrier gas flow at 44 mL/min flow rate. For a 2-mm I.D. column, set the temperature at 100°C isothermal. For a 4-mm I.D. column, set the temperature at 150°C isothermal.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external standard calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.4 If cleanup is performed on the samples, the analyst should process a series of standards through the cleanup procedure and then analyze the samples by GC. This will confirm elution patterns and the absence of interferents from the reagents.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence when using FID and after each group of 5 samples in the analysis sequence when using ECD.

7.4.3 An example of a GC/FID chromatogram for nitrobenzene and isophorone is shown in Figure 1. Figure 2 is an example of a GC/ECD chromatogram of the dinitrotoluenes.

7.4.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each analyte peak in the sample chromatogram. See Section 7.8 of Method 8000 for calculation equations.

7.4.6 If peak detection and identification are prevented due to interferences, the hexane extract may undergo cleanup using Method 3620.

7.5 Cleanup:

7.5.1 Proceed with Method 3620, using the 2-mL hexane extracts obtained from either Paragraph 7.1.3.5 or 7.1.4.3.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each parameter of interest in acetone at a concentration of 20 ug/mL for each dinitrotoluene and 100 ug/mL for isophorone and nitrobenzene.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

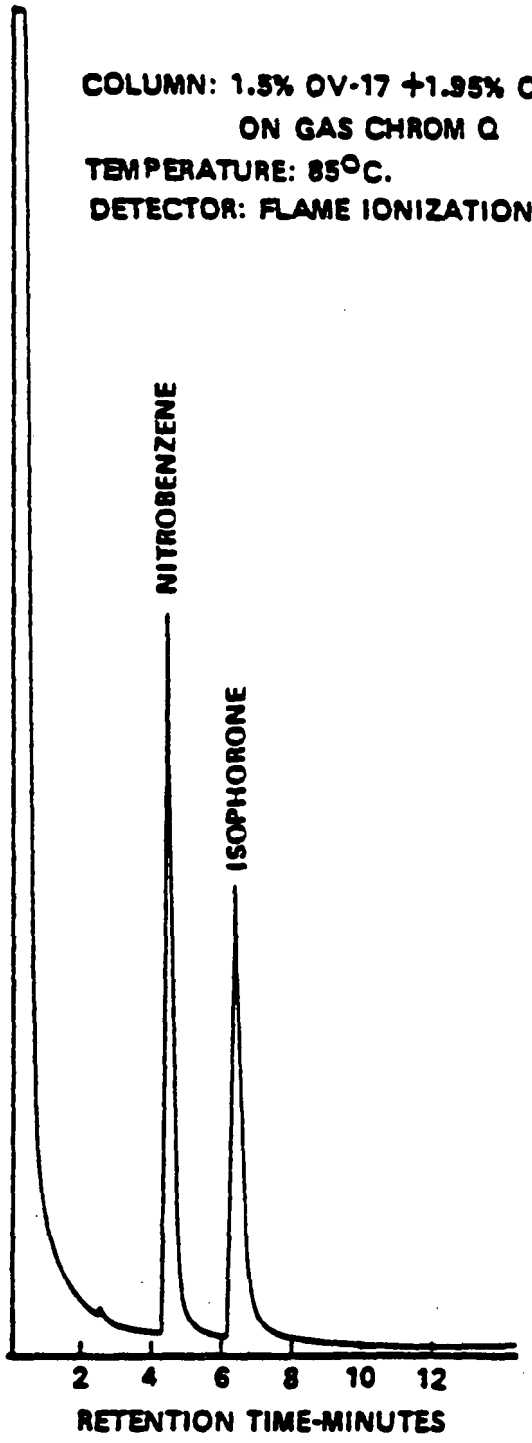


Figure 1. Gas chromatogram of nitrobenzene and isophorone.

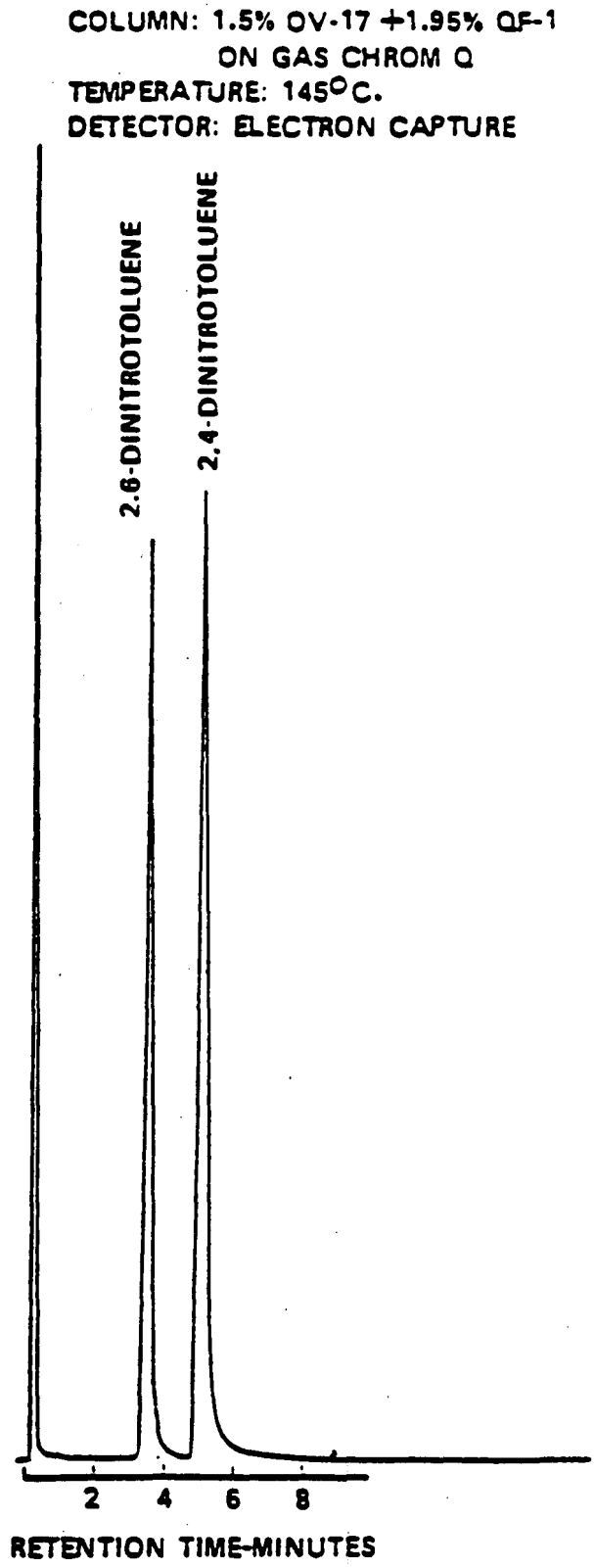


Figure 2. Gas chromatogram of dinitrotoluenes.

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 The method was tested by 18 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 1.0 to 515 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 4 - Nitroaromatics and Isophorone,' Report for EPA Contract 68-03-2624 (in preparation).

2. "Determination of Nitroaromatics and Isophorone in Industrial and Municipal Wastewaters," EPA-600/4-82-024, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, June 1982.

3. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

4. "EPA Method Validation Study 19, Method 609 (Nitroaromatics and Isophorone)," Report for EPA Contract 68-03-2624 (in preparation).

5. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

6. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

TABLE 3. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_S (%)
2,4-Dinitrotoluene	20	5.1	3.6-22.8	6-125
2,6-Dinitrotoluene	20	4.8	3.8-23.0	8-126
Isophorone	100	32.3	8.0-100.0	D-117
Nitrobenzene	100	33.3	25.7-100.0	6-118

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_S = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 609. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

TABLE 4. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
2,4-Dinitrotoluene	0.65C+0.22	0.20$\bar{X}$+0.08	0.37$\bar{X}$-0.07
2,4-Dinitrotoluene	0.66C+0.20	0.19$\bar{X}$+0.06	0.36$\bar{X}$-0.00
Isophorene	0.49C+2.93	0.28$\bar{X}$+2.77	0.46$\bar{X}$+0.31
Nitrobenzene	0.60C+2.00	0.25$\bar{X}$+2.53	0.37$\bar{X}$-0.78

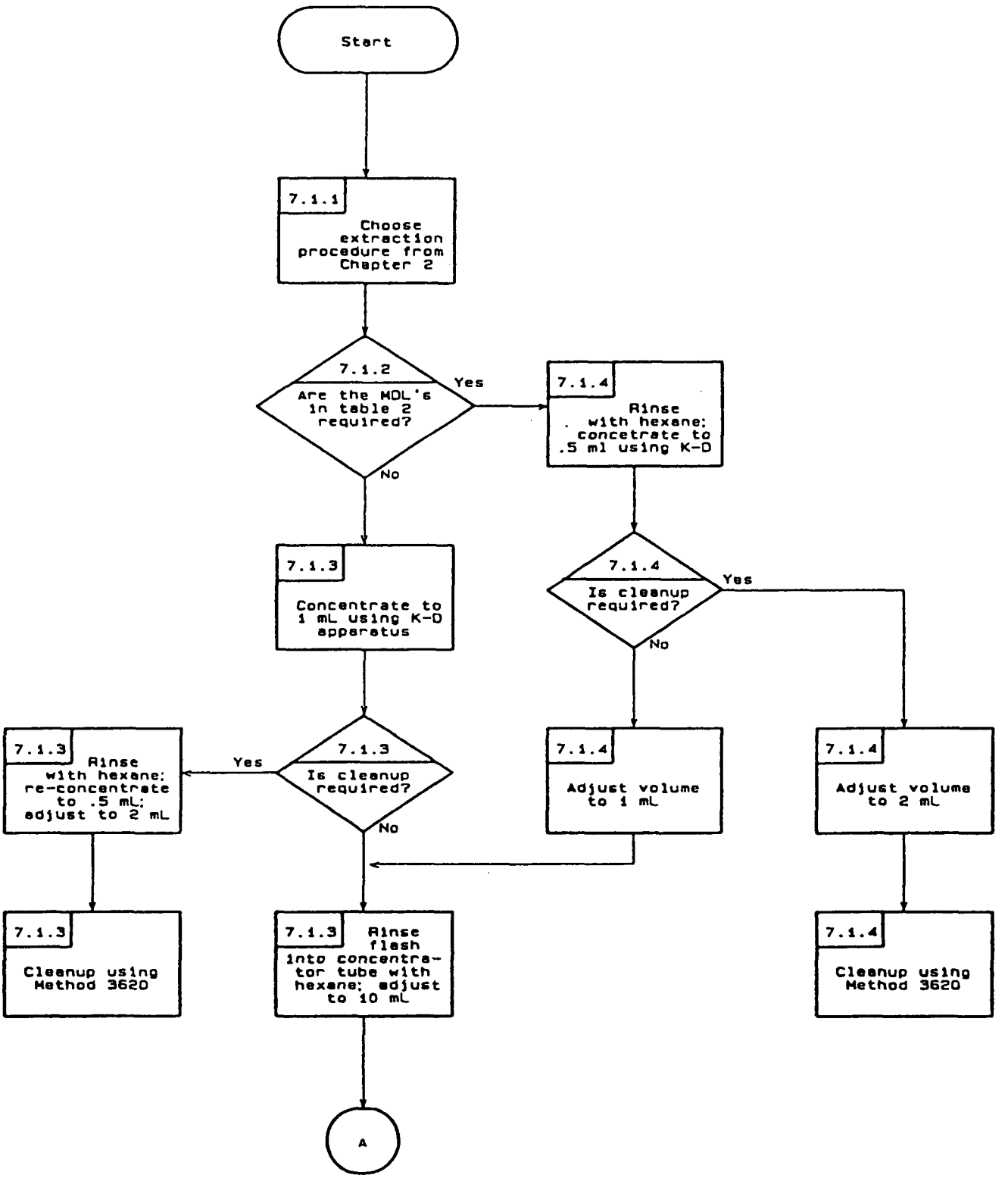
x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

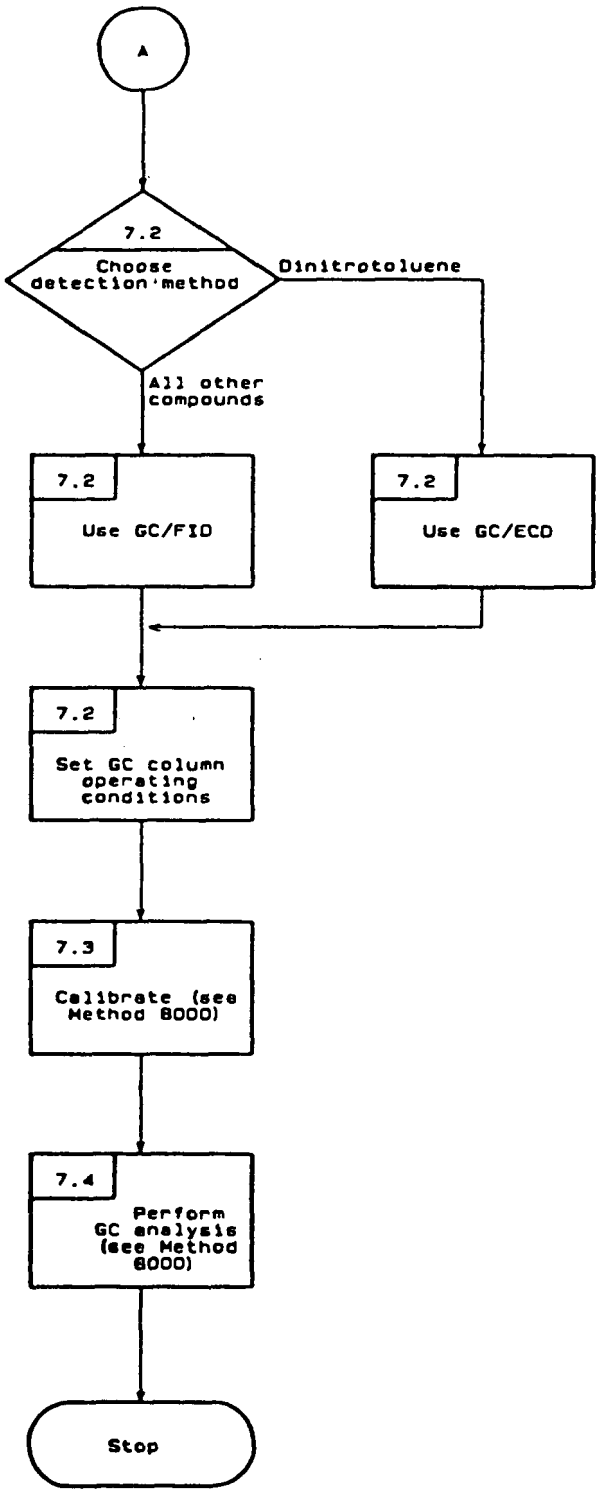
s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.


Start
7.1.1
Choose extraction procedure from Chapter 2
7.1.2
Are the MDL's in table 2 required?
Yes
No
7.1.4
Rinse with hexane; concetrate to .5 ml using K-D
7.1.3
Concentrate to 1 mL using K-D apparatus
7.1.4
Is cleanup required?
Yes
No
7.1.3
Is cleanup required?
Yes
No
7.1.3
Rinse with hexane; re-concentrate to .5 mL; adjust to 2 mL
7.1.4
Adjust volume to 1 mL
7.1.4
Adjust volume to 2 mL
7.1.3
Cleanup using Method 3620
7.1.3
Rinse flash into concentrator tube with hexane; adjust to 10 mL
7.1.4
Cleanup using Method 3620
A


A
7.2
Choose detection method
Dinitrotoluene
All other compounds
7.2
Use GC/FID
7.2
Use GC/ECD
7.2
Set GC column operating conditions
7.3
Calibrate (see Method 8000)
7.4
Perform GC analysis (see Method 8000)
Stop

METHOD 8100

POLYNUCLEAR AROMATIC HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 Method 8100 is used to determine the concentration of certain polynuclear aromatic hydrocarbons (PAH). Table 1 indicates compounds that may be determined by this method.

1.2 The packed column gas chromatographic method described here cannot adequately resolve the following four pairs of compounds: anthracene and phenanthrene; chrysene and benzo(a)anthracene; benzo(b)fluoranthene and benzo(k)fluoranthene; and dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene. The use of a capillary column instead of the packed column, also described in this method, may adequately resolve these PAHs. However, unless the purpose of the analysis can be served by reporting a quantitative sum for an unresolved PAH pair, either liquid chromatography (Method 8310) or gas chromatography/mass spectroscopy (Method 8270) should be used for these compounds.

2.0 SUMMARY OF METHOD

2.1 Method 8100 provides gas chromatographic conditions for the detection of ppb levels of certain polynuclear aromatic hydrocarbons. Prior to use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL aliquot of the extract is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by a flame ionization detector (FID).

2.2 If interferences prevent proper detection of the analytes of interest, the method may also be performed on extracts that have undergone cleanup using silica gel column cleanup (Method 3630).

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.3 Interferences coextracted from samples will vary considerably from source to source, depending upon the waste being sampled. Although general cleanup techniques are recommended as part of this method, unique samples may require additional cleanup.

TABLE 1. GAS CHROMATOGRAPHY OF POLYNUCLEAR AROMATIC HYDROCARBONS[a]

Compound	Retention time (min)
Acenaphthene	10.8
Acenaphthylene	10.4
Anthracene	15.9
Benzo(a)anthracene	20.6
Benzo(a)pyrene	29.4
Benzo(b)fluoranthene	28.0
Benzo(j)fluoranthene	
Benzo(k)fluoranthene	28.0
Benzo(ghi)perylene	38.6
Chrysene	24.7
Dibenz(a,h)acridine	
Dibenz(a,j)acridine	
Dibenzo(a,h)anthracene	36.2
7H-Dibenzo(c,g)carbazole	
Dibenzo(a,e)pyrene	
Dibenzo(a,h)pyrene	
Dibenzo(a,i)pyrene	
Fluoranthene	19.8
Fluorene	12.6
Indeno(1,2,3-cd)pyrene	36.2
3-Methylcholanthrene	
Naphthalene	4.5
Phenanthrene	15.9
Pyrene	20.6

[a]Results obtained using Column 1.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph:

4.1.1 **Gas chromatograph:** Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.2 **Columns:**

4.1.2.1 Column 1: 1.8-m x 2-mm I.D. glass column packed with 3% OV-17 on Chromosorb W-AW-DCMS (100/120 mesh) or equivalent.

4.1.2.2 Column 2: 30-m x 0.25-mm I.D. SE-54 fused silica capillary column.

4.1.2.3 Column 3: 30-m x 0.32-mm I.D. SE-54 fused silica capillary column.

4.1.3 **Detector:** Flame ionization (FID).

4.2 Volumetric flask: 10-, 50-, and 100-mL, ground-glass stopper.

4.3 Microsyringe: 10-uL.

5.0 REAGENTS

5.1 Solvents: Hexane, isooctane (2,2,4-trimethylpentane) (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in isooctane and diluting to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared through dilution of the stock standards with isooctane. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with a check standard indicates a problem.

5.4 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two surrogates (e.g., 2-fluorobiphenyl and 1-fluoronaphthalene) recommended to encompass the range of the temperature program used in this method. Method 3500, Section 5.3.1.1, details instructions on the preparation of base/neutral surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and must be analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550. To achieve maximum sensitivity with this method, the extract must be concentrated to 1 mL.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1:** Set nitrogen carrier gas flow at 40-mL/min flow rate. Set column temperature at 100°C for 4 min; then program at 8°C/min to a final hold at 280°C.

7.2.2 **Column 2:** Set helium carrier gas at 20-cm/sec flow rate. Set column temperature at 35°C for 2 min; then program at 10°C/min to 265°C and hold for 12 min.

7.2.3 **Column 3:** Set helium carrier gas at 60 cm/sec flow rate. Set column temperature at 35°C for 2 min; then program at 10°C/min to 265°C and hold for 3 min.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques.

7.3.1 The procedure for internal or external standard calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 If cleanup is performed on the samples, the analyst should process a series of standards through the cleanup procedure and then analyze the samples by GC. This will validate elution patterns and the absence of interferents from the reagents.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.4 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Section 7.8 of Method 8000 for calculation equations.

7.4.5 If peak detection and identification are prevented due to interferences, the extract may undergo cleanup using Method 3630.

7.5 Cleanup:

7.5.1 Proceed with Method 3630. Instructions are given in this method for exchanging the solvent of the extract to hexane.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 ug/mL; acenaphthylene, 100 ug/mL; acenaphthene, 100 ug/mL; fluorene, 100 ug/mL; phenanthrene, 100 ug/mL; anthracene, 100 ug/mL; benzo(k)fluoranthene, 5 ug/mL; and any other PAH at 10 ug/mL.

8.2.2 Table 2 indicates the calibration and QC acceptance criteria for this method. Table 3 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 The method was tested by 16 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 0.1 to 425 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to

the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 3.

9.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 8 x MDL to 800 x MDL with the following exception: benzo(ghi)perylene recovery at 80 x and 800 x MDL were low (35% and 45%, respectively).

9.3 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 9 - PAHs," Report for EPA Contract 68-03-2624 (in preparation).

2. Sauter, A.D., L.D. Betowski, T.R. Smith, V.A. Strickler, R.G. Beimer, B.N. Colby, and J.E. Wilkinson, "Fused Silica Capillary Column GC/MS for the Analysis of Priority Pollutants," Journal of HRC&CC 4, 366-384, 1981.

3. "Determination of Polynuclear Aromatic Hydrocarbons in Industrial and Municipal Wastewaters," EPA-600/4-82-025, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, September 1982.

4. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

5. "EPA Method Validation Study 20, Method 610 (Polynuclear Aromatic Hydrocarbons)," Report for EPA Contract 68-03-2624 (in preparation).

6. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

7. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

TABLE 2. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_s (%)
Acenaphthene	100	40.3	D-105.7	D-124
Acenaphthylene	100	45.1	22.1-112.1	D-139
Anthracene	100	28.7	11.2-112.3	D-126
Benzo(a)anthracene	10	4.0	3.1-11.6	12-135
Benzo(a)pyrene	10	4.0	0.2-11.0	D-128
Benzo(b)fluoranthene	10	3.1	1.8-13.8	6-150
Benzo(ghi)perylene	10	2.3	D-10.7	D-116
Benzo(k)fluoranthene	5	2.5	D-7.0	D-159
Chrysene	10	4.2	D-17.5	D-199
Dibenzo(a,h)anthracene	10	2.0	0.3-10.0	D-110
Fluoranthene	10	3.0	2.7-11.1	14-123
Fluorene	100	43.0	D-119	D-142
Indeno(1,2,3-cd)pyrene	10	3.0	1.2-10.0	D-116
Naphthalene	100	40.7	21.5-100.0	D-122
Phenanthrene	100	37.7	8.4-133.7	D-155
Pyrene	10	3.4	1.4-12.1	D-140

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 610. These criteria are based directly upon the method performance data in Table 3. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 3.

TABLE 3. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Acenaphthene	0.52C+0.54	0.39$\bar{X}$+0.76	0.53$\bar{X}$+1.32
Acenaphthylene	0.69C-1.89	0.36$\bar{X}$+0.29	0.42$\bar{X}$+0.52
Anthracene	0.63C-1.26	0.23$\bar{X}$+1.16	0.41$\bar{X}$+0.45
Benzo(a)anthracene	0.73C+0.05	0.28$\bar{X}$+0.04	0.34$\bar{X}$+0.02
Benzo(a)pyrene	0.56C+0.01	0.38$\bar{X}$-0.01	0.53$\bar{X}$-0.01
Benzo(b)fluoranthene	0.78C+0.01	0.21$\bar{X}$+0.01	0.38$\bar{X}$-0.00
Benzo(ghi)perylene	0.44C+0.30	0.25$\bar{X}$+0.04	0.58$\bar{X}$+0.10
Benzo(k)fluoranthene	0.59C+0.00	0.44$\bar{X}$-0.00	0.69$\bar{X}$+0.10
Chrysene	0.77C-0.18	0.32$\bar{X}$-0.18	0.66$\bar{X}$-0.22
Dibenzo(a,h)anthracene	0.41C-0.11	0.24$\bar{X}$+0.02	0.45$\bar{X}$+0.03
Fluoranthene	0.68C+0.07	0.22$\bar{X}$+0.06	0.32$\bar{X}$+0.03
Fluorene	0.56C-0.52	0.44$\bar{X}$-1.12	0.63$\bar{X}$-0.65
Ideno(1,2,3-cd)pyrene	0.54C+0.06	0.29$\bar{X}$+0.02	0.42$\bar{X}$+0.01
Naphthalene	0.57C-0.70	0.39$\bar{X}$-0.18	0.41$\bar{X}$+0.74
Phenanthrene	0.72C-0.95	0.29$\bar{X}$+0.05	0.47$\bar{X}$-0.25
Pyrene	0.69C-0.12	0.25$\bar{X}$+0.14	0.42$\bar{X}$-0.00

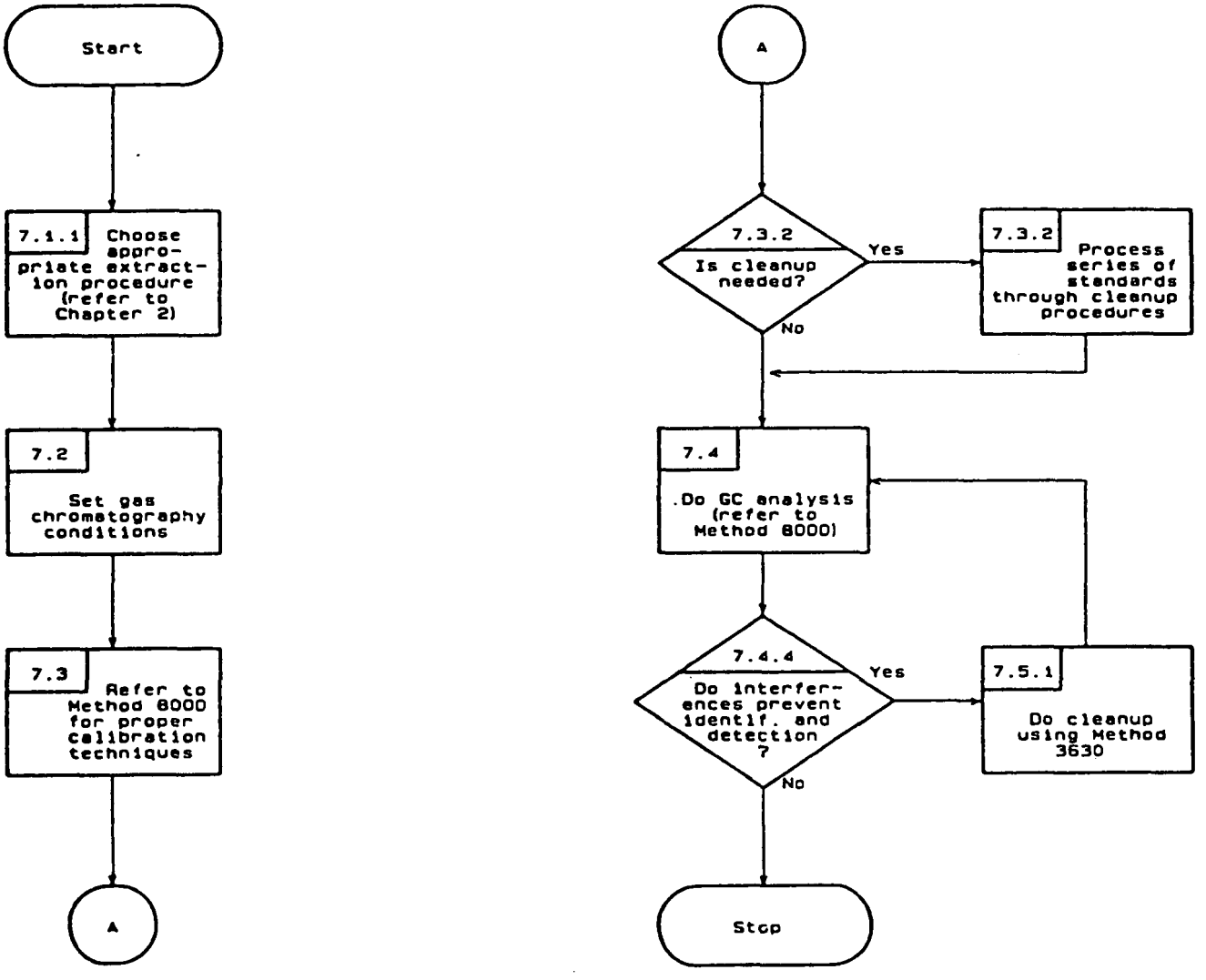
x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.


Start
7.1.1 Choose appropriate extraction procedure (refer to Chapter 2)
7.2 Set gas chromatography conditions
7.3 Refer to Method 8000 for proper calibration techniques
A
A
7.3.2 Is cleanup needed?
Yes
No
7.3.2 Process series of standards through cleanup procedures
7.4 Do GC analysis (refer to Method 8000)
7.4.4 Do interferences prevent identif. and detection ?
Yes
No
7.5.1 Do cleanup using Method 3630
Stop

METHOD 8120

CHLORINATED HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 Method 8120 is used to determine the concentration of certain chlorinated hydrocarbons. Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8120 provides gas chromatographic conditions for the detection of ppb levels of certain chlorinated hydrocarbons. Prior to use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL aliquot of the extract is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD).

2.2 If interferences are encountered in the analysis, Method 8120 may also be performed on extracts that have undergone cleanup using Method 3620.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.3 Interferences coextracted from samples will vary considerably from source to source, depending upon the waste being sampled. Although general cleanup techniques are recommended as part of this method, unique samples may require additional cleanup.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph:

4.1.1 **Gas chromatograph:** Analytical system complete with gas chromatograph suitable for on-column injections and all required

TABLE 1. GAS CHROMATOGRAPHY OF CHLORINATED HYDROCARBONS

Compound	Retention time (min) Col. 1	Retention time (min) Col. 2	$	Method Detection limit (ug/L)
Benzal chloride				
Benzotrichloride				
Benzyl chloride				
2-Chloronaphthalene	2.7[a]	3.6[b]		0.94
1,2-Dichlorobenzene	6.6	9.3		1.14
1,3-Dichlorobenzene	4.5	6.8		1.19
1,4-Dichlorobenzene	5.2	7.6		1.34
Hexachlorobenzene	5.6[a]	10.1[b]		0.05
Hexachlorobutadiene	7.7	20.0		0.34
Hexachlorocyclohexane				
Hexachlorocyclopentadiene	nd	16.5[c]		0.40
Hexachloroethane	4.9	8.3		0.03
Tetrachlorobenzenes				
1,2,4-Trichlorobenzene	15.5	22.3		0.05
Pentachlorohexane				

nd = not determined.

[a]150°C column temperature.

[b]165°C column temperature.

[c]100°C column temperature.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.2 **Columns:**

4.1.2.1 Column 1: 1.8-m x 2-mm I.D. glass column packed with 1% SP-1000 on Supelcoport (100/120 mesh) or equivalent.

4.1.2.2 Column 2: 1.8-m x 2-mm I.D. glass column packed with 1.5% OV-1/2.4% OV-225 on Supelcoport (80/100 mesh) or equivalent.

4.1.3 **Detector:** Electron capture (ECD).

4.2 Kuderna-Danish (K-D) apparatus:

4.2.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts

4.2.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.2.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.4 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.5 Volumetric flasks: 10-, 50-, and 100-mL, ground-glass stopper.

4.6 Microsyringe: 10-uL.

4.7 Syringe: 5-mL.

4.8 Vials: Glass, 2-, 10-, and 20-mL capacity with Teflon-lined screw cap.

5.0 REAGENTS

5.1 Solvents: hexane, isooctane, acetone (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in isooctane and diluting to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared through dilution of the stock standards with isooctane. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.4 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two surrogates (e.g., chlorinated hydrocarbons that are not expected to be in the sample) recommended to encompass the range of the temperature program used in this method. Method 3500, Section 5.3.1.1, details instructions on the preparation of base/neutral surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1-mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.2.2 Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. The extract will be handled differently at this point, depending on whether or not cleanup is needed. If cleanup is not required, proceed to Paragraph 7.1.2.3. If cleanup is needed, proceed to Paragraph 7.1.2.4.

7.1.2.3 If cleanup of the extract is not required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with gas chromatographic analysis.

7.1.2.4 If cleanup of the extract is required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with a minimum amount of hexane. A 5-mL syringe is recommended for this operation. Add a clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding about 0.5 mL of hexane to the top. Place the micro-K-D apparatus on the water bath (80°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.2.5 Remove the micro-Snyder column and rinse the flask and its lower joint into the concentrator tube with 0.2 mL of hexane. Adjust the extract volume to 2.0 mL and proceed with Method 3620.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1:** Set 5% methane/95% argon carrier gas flow at 25 mL/min flow rate. Set column temperature at 65°C isothermal, unless otherwise specified (see Table 1).

7.2.2 **Column 2:** Set 5% methane/95% argon carrier gas flow at 25 mL/min flow rate. Set column temperature at 75°C isothermal, unless otherwise specified (see Table 1).

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 If cleanup is performed on the samples, the analyst should process a series of standards through the cleanup procedure and then analyze the samples by GC. This will validate elution patterns and the absence of interferents from the reagents.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injecting.

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Examples of GC/ECD chromatograms for certain chlorinated hydrocarbons are shown in Figures 1 and 2.

7.4.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.4 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Section 7.8 of Method 8000 for calculation equations.

7.4.5 If peak detection and identification are prevented due to interferences, the hexane extract may undergo cleanup using Method 3620.

7.5 Cleanup:

7.5.1 Proceed with Method 3620 using the 2-mL hexane extracts obtained from Paragraph 7.1.2.5.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each parameter of interest at the following concentrations in acetone: hexachloro-substituted hydrocarbon, 10 ug/mL; and any other chlorinated hydrocarbon, 100 ug/mL.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

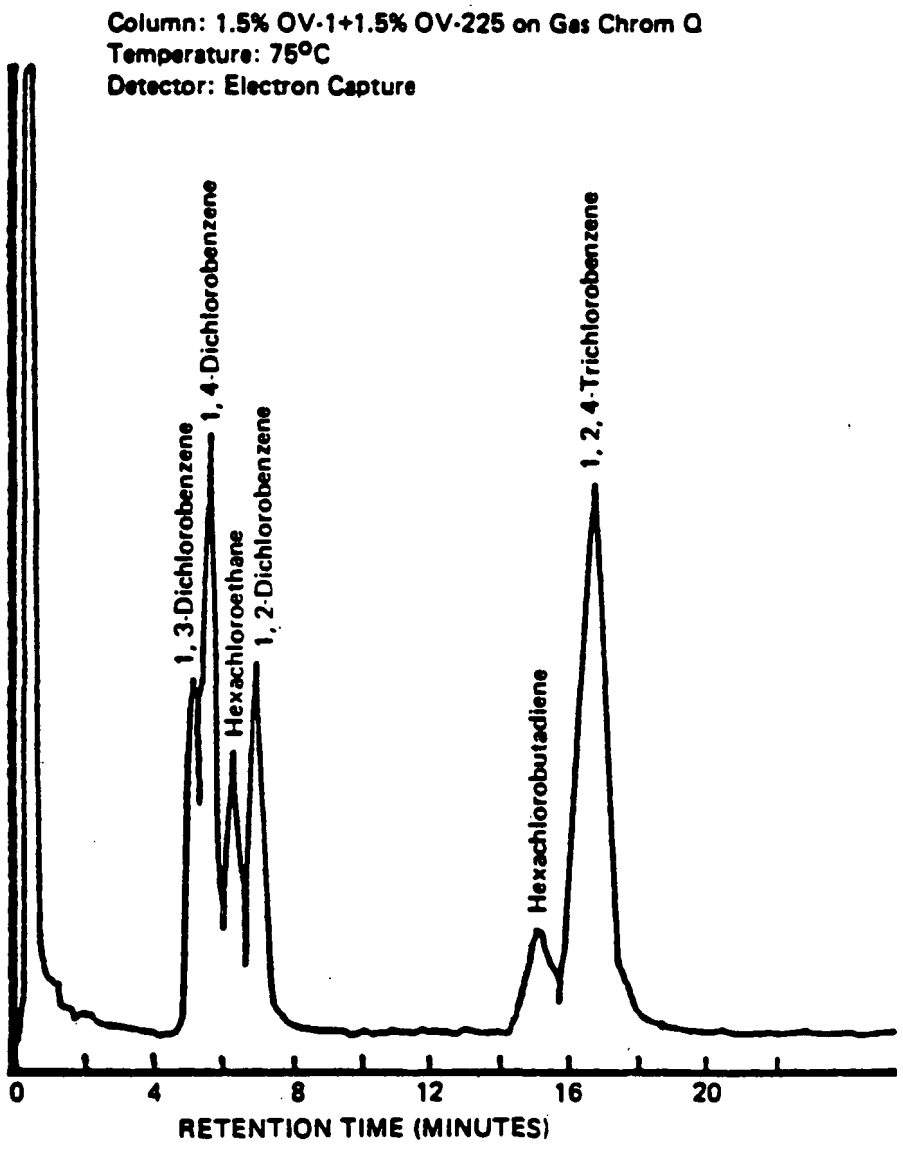


Figure 1. Gas chromatogram of chlorinated hydrocarbons (low molecular weight compounds).

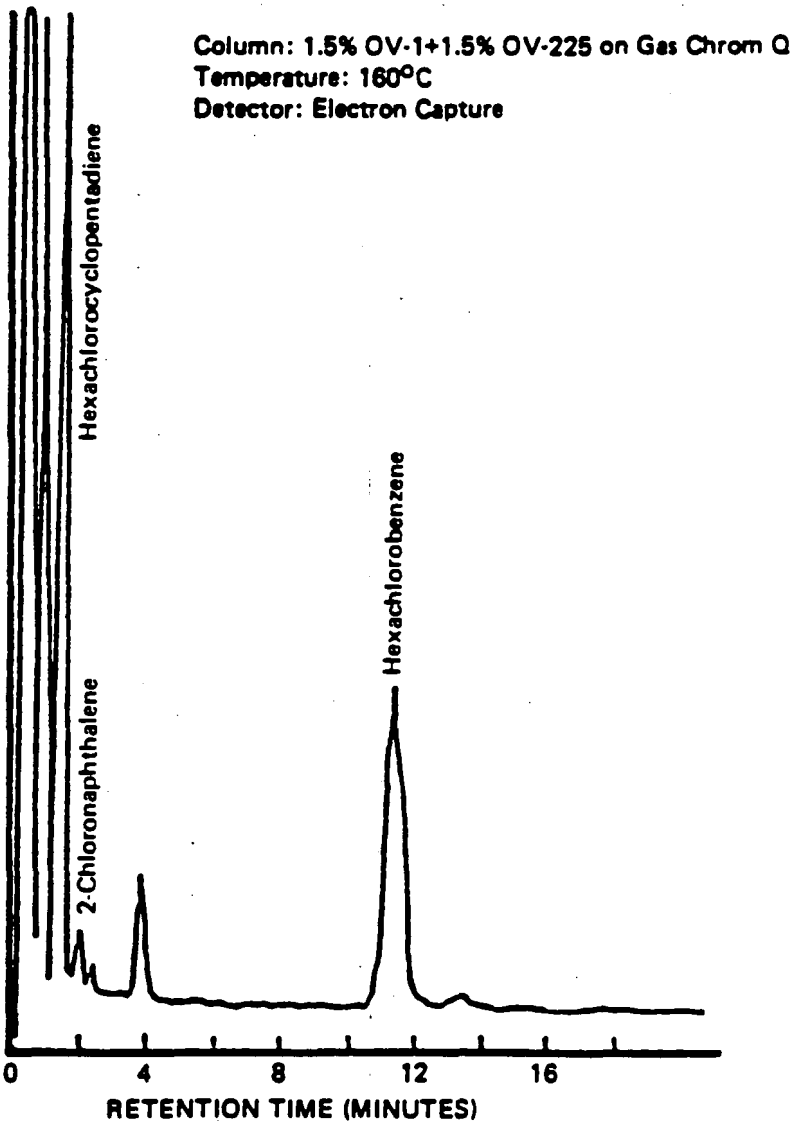


Figure 2. Gas chromatogram of chlorinated hydrocarbons (high molecular weight compounds).

8.3.1 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 The method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 1.0 to 356 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 3 - Chlorinated Hydrocarbons, and Category 8 - Phenols," Report for EPA Contract 68-03-2625 (in preparation).

2. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

3. "EPA Method Validation Study 22, Method 612 (Chlorinated Hydrocarbons)," Report for EPA Contract 68-03-2625 (in preparation).

4. "Method Performance for Hexachlorocyclopentadiene by Method 612," Memorandum from R. Slater, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, December 7, 1983.

5. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

6. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

7. "Determination of Chlorinated Hydrocarbons in Industrial and Municipal Wastewaters," Report for EPA Contract 68-03-2625 (in preparation).

TABLE 3. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_s (%)
2-Chloronaphthalene	100	37.3	29.5-126.9	9-148
1,2-Dichlorobenzene	100	28.3	23.5-145.1	9-160
1,3-Dichlorobenzene	100	26.4	7.2-138.6	D-150
1,4-Dichlorobenzene	100	20.8	22.7-126.9	13-137
Hexachlorobenzene	10	2.4	2.6-14.8	15-159
Hexachlorobutadiene	10	2.2	D-12.7	D-139
Hexachlorocyclopentadiene	10	2.5	D-10.4	D-111
Hexachloroethane	10	3.3	2.4-12.3	8-139
1,2,4-Trichlorobenzene	100	31.6	20.2-133.7	5-149

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 612. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

Table 4. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Chloronaphthalene	0.75C+3.21	0.28$\bar{X}$-1.17	0.38$\bar{X}$-1.39
1,2-Dichlorobenzene	0.85C-0.70	0.22$\bar{X}$-2.95	0.41$\bar{X}$-3.92
1,3-Dichlorobenzene	0.72C+0.87	0.21$\bar{X}$-1.03	0.49$\bar{X}$-3.98
1,4-Dichlorobenzene	0.72C+2.80	0.16$\bar{X}$-0.48	0.35$\bar{X}$-0.57
Hexachlorobenzene	0.87C-0.02	0.14$\bar{X}$+0.07	0.36$\bar{X}$-0.19
Hexachlorobutadiene	0.61C+0.03	0.18$\bar{X}$+0.08	0.53$\bar{X}$-0.12
Hexachlorocyclopentadiene[a]	0.47C	0.24$\bar{X}$	0.50$\bar{X}$
Hexachloroethane	0.74C-0.02	0.23$\bar{X}$+0.07	0.36$\bar{X}$-0.00
1,2,4-Trichlorobenzene	0.76C+0.98	0.23$\bar{X}$-0.44	0.40$\bar{X}$-1.37

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

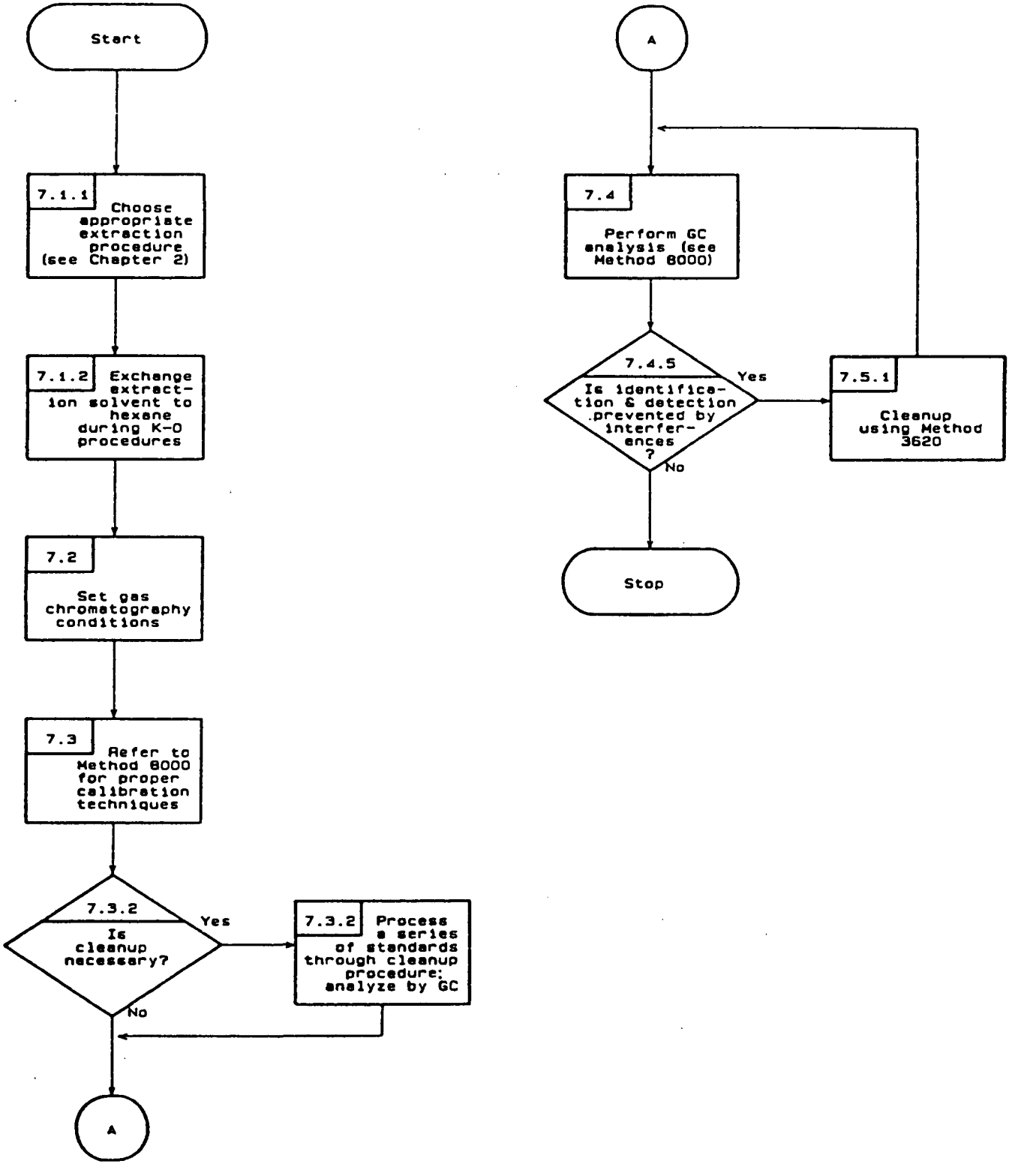
s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.

[a]Estimates based upon the performance in a single laboratory.


Start
7.1.1 Choose appropriate extraction procedure (see Chapter 2)
7.1.2 Exchange extraction solvent to hexane during K-D procedures
7.2 Set gas chromatography conditions
7.3 Refer to Method 8000 for proper calibration techniques
7.3.2 Is cleanup necessary?
Yes
7.3.2 Process a series of standards through cleanup procedure; analyze by GC
No
A
A
7.4 Perform GC analysis (see Method 8000)
7.4.5 Is identification & detection prevented by interferences ?
Yes
7.5.1 Cleanup using Method 3620
No
Stop

METHOD 8140

ORGANOPHOSPHORUS PESTICIDES

1.0 SCOPE AND APPLICATION

1.1 Method 8140 is a gas chromatographic (GC) method used to determine the concentration of various organosphosphorus pesticides. Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

1.2 When Method 8140 is used to analyze unfamiliar samples, compound identifications should be supported by at least two additional qualitative techniques if mass spectroscopy is not employed. Section 8.4 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

2.0 SUMMARY OF METHOD

2.1 Method 8140 provides gas chromatographic conditions for the detection of ppb levels of organophosphorus pesticides. Prior to analysis, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL aliquot of the extract is injected into a gas chromatograph, and compounds in the GC effluent are detected with a flame photometric or thermionic detector.

2.2 If interferences are encountered in the analysis, Method 8140 may also be performed on extracts that have undergone cleanup using Method 3620 and/or Method 3660.

3.0 INTERFERENCES

3.1 Refer to Methods 3500 (Section 3.5, in particular), 3600, and 8000.

3.2 The use of Florisil cleanup materials (Method 3620) for some of the compounds in this method has been demonstrated to yield recoveries less than 85% and is therefore not recommended for all compounds. Refer to Table 2 of Method 3620 for recoveries of organophosphorous pesticides as a function of Florisil fractions. Use of phosphorus- or halogen-specific detectors, however, often obviates the necessity for cleanup for relatively clean sample matrices. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each analyte is no less than 85%.

TABLE 1. GAS CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS FOR ORGANOPHOSPHOROUS PESTICIDES[a]

Compound	GC column[b]	Retention time (min)	Method detection limit (ug/L)
Azinphos methyl	1a	6.80	1.5
Bolstar	1a	4.23	0.15
Chlorpyrifos	2	6.16	0.3
Coumaphos	1a	11.6	1.5
Demeton-O	1a	2.53	0.25
Demeton-S	1a	1.16	0.25
Diazinon	2	7.73	0.6
Dichlorvos	1b, 3	0.8, 1.50	0.1
Disulfoton	1a	2.10	0.20
Ethoprop	2	3.02	0.25
Fensulfothion	1a	6.41	1.5
Fenthion	1a	3.12	0.10
Merphos	2	7.45	0.25
Mevinphos	1b	2.41	0.3
Naled	3	3.28	0.1
Parathion methyl	2	3.37	0.03
Phorate	1a	1.43	0.15
Ronnel	2	5.57	0.3
Stirophos (Tetrachlorvinphos)	1b, 3	8.52, 5.51	5.0
Tokuthion (Prothiofos)	1a	3.40	0.5
Trichloronate	1a	2.94	0.15

[a]Development of Analytical Test Procedures for Organic Pollutants in Wastewater; Report for EPA Contract 68-03-2711 (in preparation).

[b]See Sections 4.2.1 and 7.2 for column descriptions and conditions.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

3.3 Use of a flame photometric detector in the phosphorus mode will minimize interferences from materials that do not contain phosphorus. Elemental sulfur, however, may interfere with the determination of certain organophosphorus pesticides by flame photometric gas chromatography. Sulfur cleanup using Method 3660 may alleviate this interference.

3.4 A halogen-specific detector (i.e., electrolytic conductivity or microcoulometric) is very selective for the halogen-containing pesticides and is recommended for use with dichlorvos, naled, and stirophos.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.1 **Columns:**

4.1.1.1 Column 1a and 1b: 1.8-m x 2-mm I.D. glass, packed with 5% SP-2401 on Supelcoport, 100/120 mesh (or equivalent).

4.1.1.2 Column 2: 1.8-m x 2-mm I.D. glass, packed with 3% SP-2401 on Supelcoport, 100/120 mesh (or equivalent).

4.1.1.3 Column 3: 50-cm x 1/8-in O.D. Teflon, packed with 15% SE-54 on Gas Chrom Q, 100/120 mesh (or equivalent).

4.1.2 **Detectors:** The following detectors have proven effective in analysis for the analytes listed in Table 1 and were used to develop the accuracy and precision statements in Section 9.0.

4.1.2.1 Phosphorus-specific: Nitrogen/Phosphorus (N/P), operated in phosphorus-sensitive mode.

4.1.2.2 Flame Photometric (FPD): FPD is more selective for phosphorus than the N/P.

4.1.2.3 Halogen-specific: Electrolytic conductivity or microcoulometric. These are very selective for those pesticides containing halogen substituents.

4.2 Balance: analytical, capable of accurately weighing to the nearest 0.0001 g.

4.3 Vials: Amber glass, 10- to 15-mL capacity with Teflon-lined screw-cap.

4.4 Kuderna-Danish (K-D) apparatus:

4.4.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts

4.4.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.4.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.4.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.5 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.6 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.7 Microsyringe: 10-uL.

4.8 Syringe: 5-mL.

4.9 Volumetric flasks: 10-, 50-, and 100-mL, ground-glass stopper.

5.0 REAGENTS

5.1 Solvents: Hexane, acetone, isooctane (2,2,4-trimethylpentane) (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in hexane or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels for each parameter of interest should be prepared through dilution of the stock standards with isooctane. One of the concentration levels should be at a concentration near, but above, the method detection

limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration standards must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.4 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with hexane or other suitable solvent.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two surrogates (e.g., organophosphorous pesticides not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent may be exchanged to hexane. This is recommended if the detector used is halogen-specific. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.2.2 Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.2.3 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with gas chromatographic analysis if further cleanup is not required.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1a:** Set helium carrier gas flow at 30 mL/min flow rate. Column temperature is set at 150°C for 1 min and then programmed at 25°C/min to 220°C and held.

7.2.2 **Column 1b:** Set nitrogen carrier gas flow at 30 mL/min flow rate. Column temperature is set at 170°C for 2 min and then programmed at 20°C/min to 220°C and held.

7.2.3 **Column 2:** Set helium carrier gas at 25 mL/min flow rate. Column temperature is set at 170°C for 7 min and then programmed at 10°C/min to 250°C and held.

7.2.4 **Column 3:** Set nitrogen carrier gas at 30 mL/min flow rate. Column temperature is set at 100°C and then immediately programmed at 25°C/min to 200°C and held.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 If cleanup is performed on the samples, the analyst should process a series of standards through the cleanup procedure and then analyze the samples by GC. This will confirm elution patterns and the absence of interferents from the reagents.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Examples of chromatograms for various organophosphorous pesticides are shown in Figures 1 through 4.

7.4.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Section 7.8 of Method 8000 for calculation equations.

7.4.6 If peak detection and identification are prevented due to interferences, the hexane extract may undergo cleanup using Method 3620. The resultant extract(s) may be analyzed by GC directly or may undergo further cleanup to remove sulfur using Method 3660.

7.5 Cleanup:

7.5.1 Proceed with Method 3620, followed by, if necessary, Method 3660, using the 10-mL hexane extracts obtained from Paragraph 7.1.2.3.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

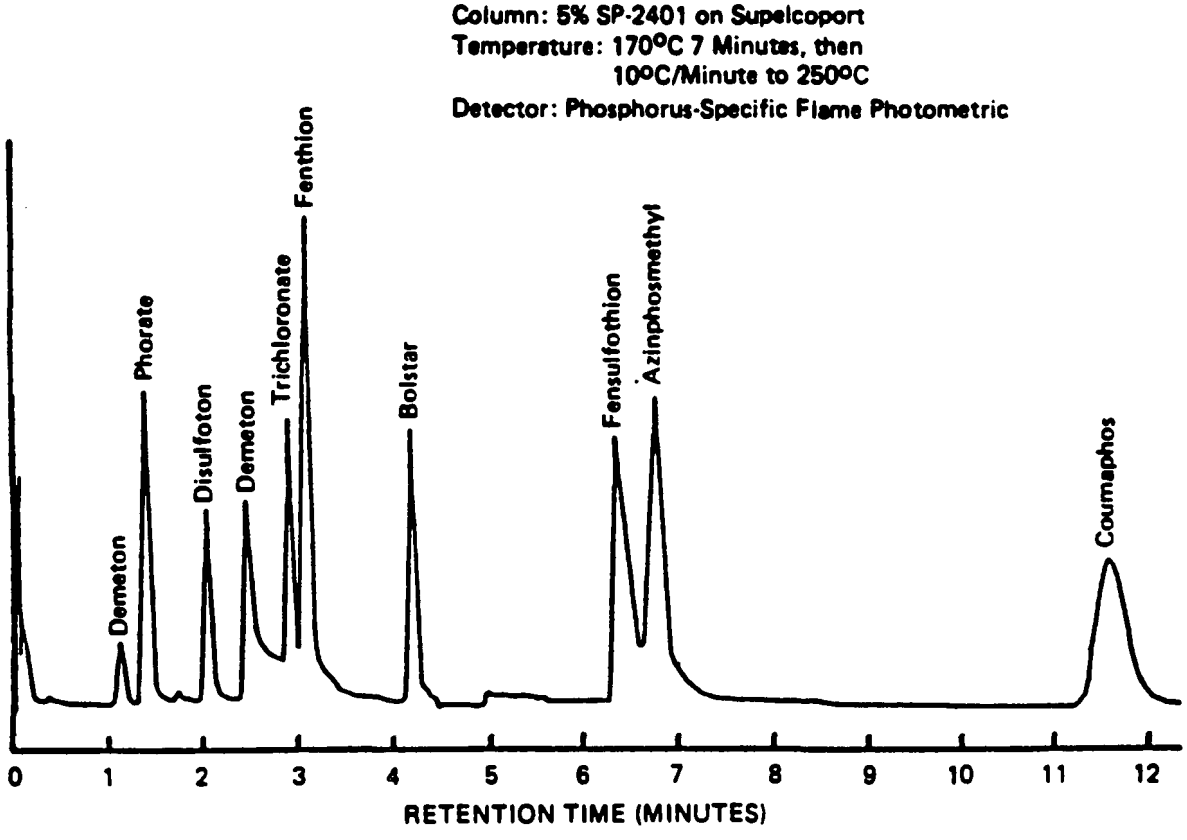


Figure 1. Gas chromatogram of organophosphorus pesticides (Example 1).

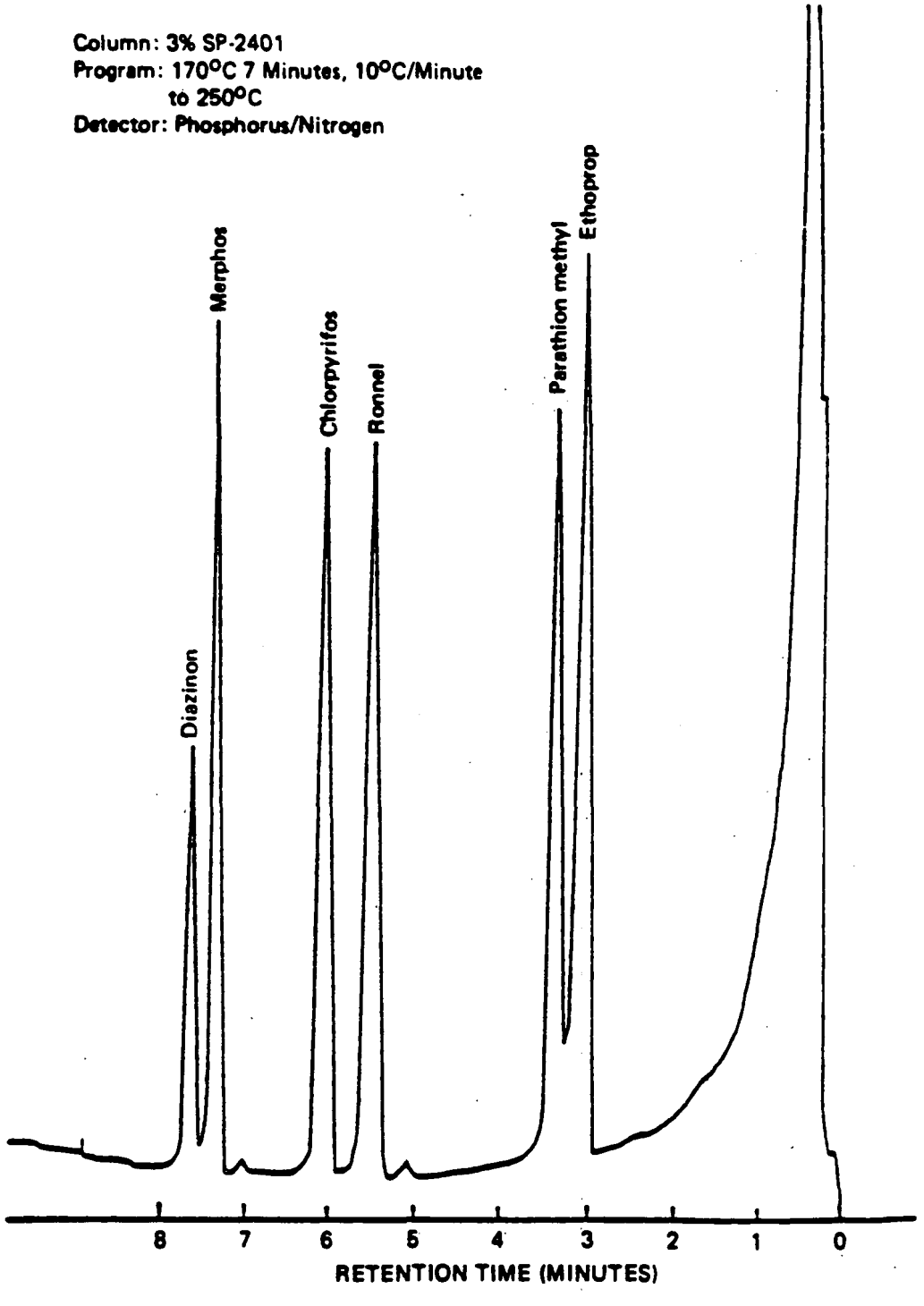


Figure 2. Gas chromatogram of organophosphorus pesticides (Example 2).

Column: 15% SE–54 on Gas Chrom Q
Temperature: 100°C Initial, then
25°C/Minute to 200°C
Detector: Hall Electrolytic Conductivity–Oxidative Mode

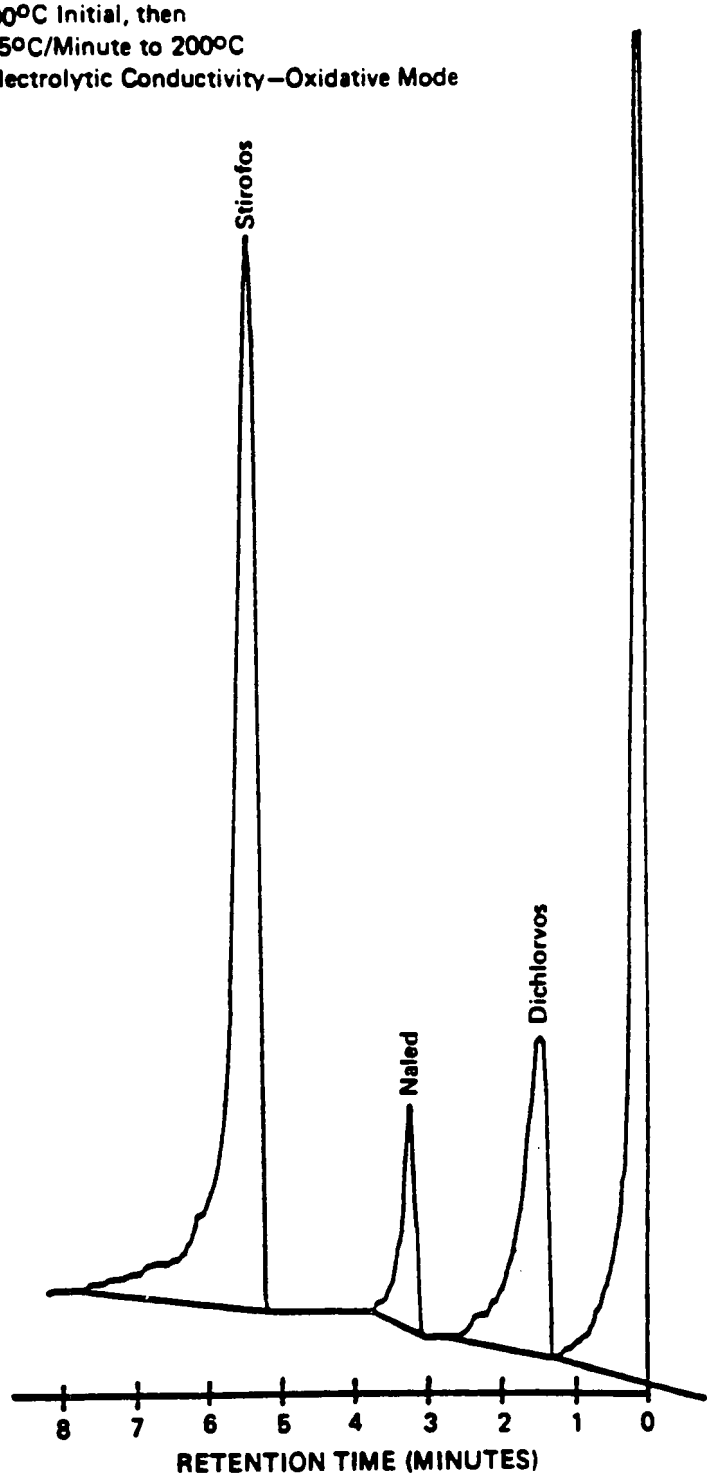


Figure 3. Gas chromatogram of organophosphorus pesticides (Example 3).

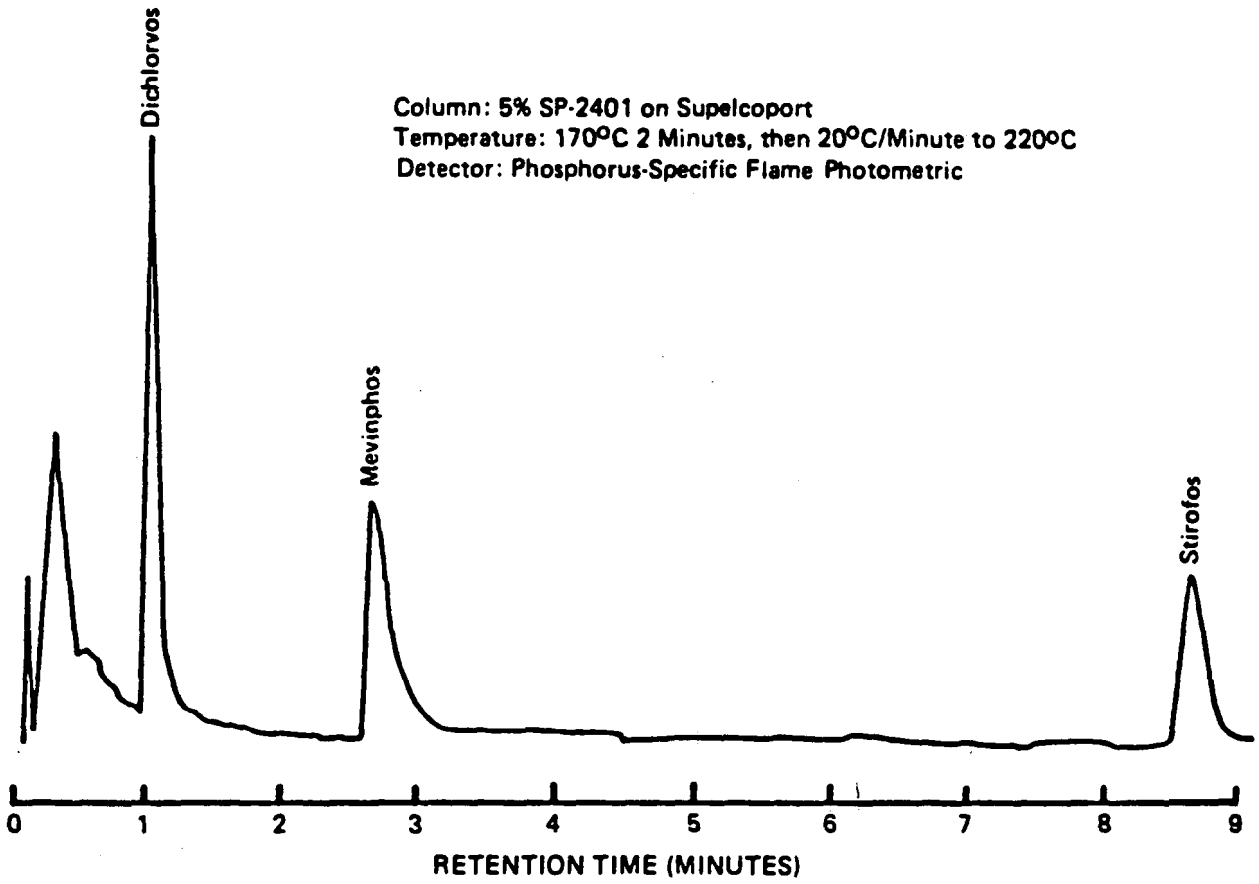


Figure 4. Gas chromatogram of organophosphorus pesticides (Example 4).

8.2.1 Select a representative spike concentration for each analyte to be measured. The quality control check sample concentrate (Method 8000, Section 8.6) should contain each analyte in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

8.2.2 Table 3 indicates Single Operator Accuracy and Precision for this method. Compare the results obtained with the results given in Table 3 to determine if the data quality is acceptable.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.4 GC/MS confirmation:

8.4.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. The GC/MS operating conditions and procedures for analysis are those specified in Method 8270.

8.4.2 When available, chemical ionization mass spectra may be employed to aid in the qualitative identification process.

8.4.3 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns and additional cleanup.

9.0 METHOD PERFORMANCE

9.1 Single-operator accuracy and precision studies have been conducted using spiked wastewater samples. The results of these studies are presented in Table 3.

10.0 REFERENCES

1. Pressley, T.A. and J.E. Longbottom, "The Determination of Organophosphorus Pesticides in Industrial and Municipal Wastewater: Method 614," U.S. EPA/EMSL, Cincinnati, OH, EPA-600/4-82-004, 1982.

2. Burke, J.A., "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists 48, 1037, 1965.

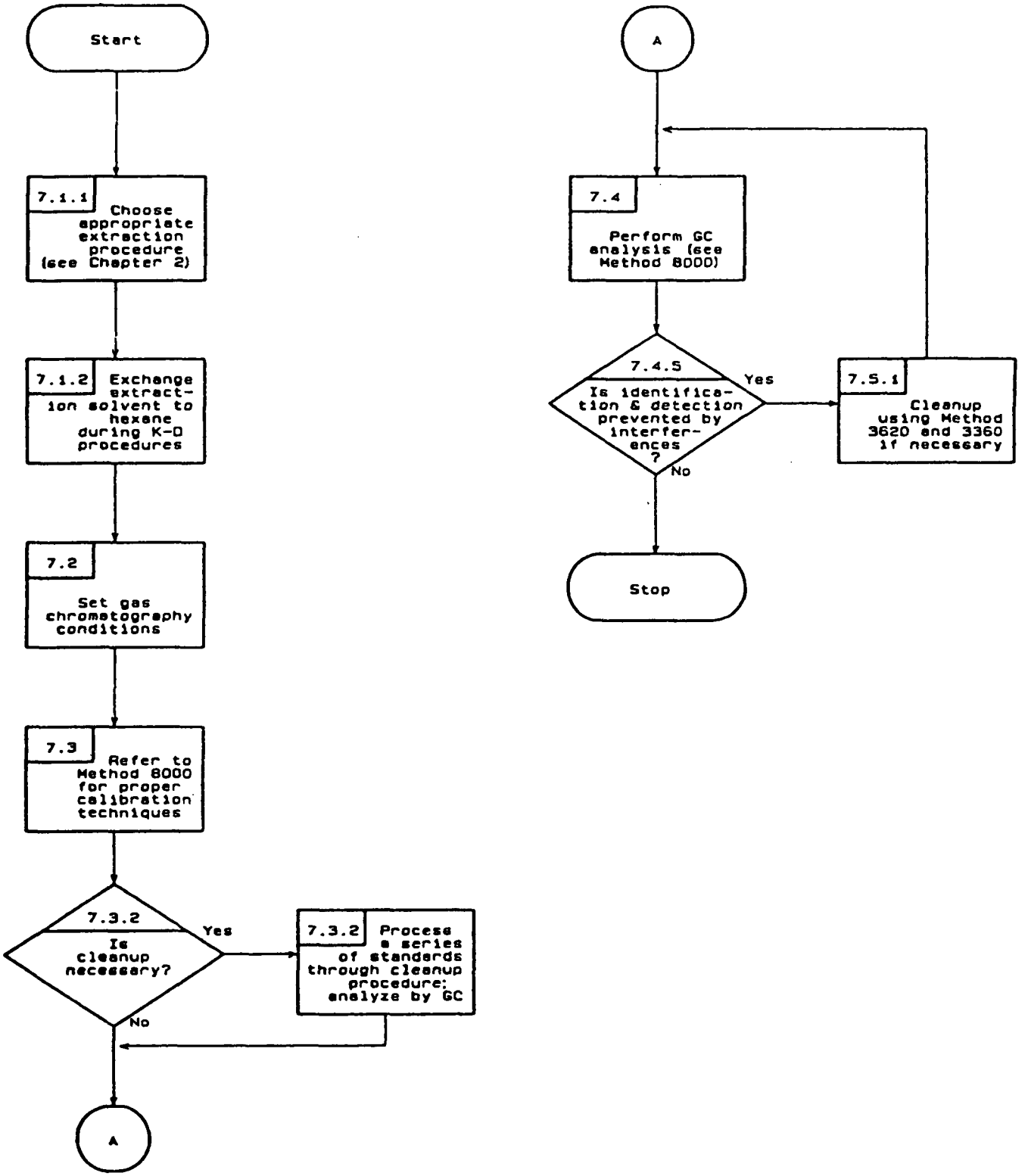
3. U.S. EPA, "Analysis of Volatile Hazardous Substances by GC/MS: Pesticide Methods Evaluation," Letter Reports 6, 12A, and 14, EPA Contract 68-03-2697, 1982.

4. U.S. EPA, "Method 622, Organophosphorous Pesticides," Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268.

TABLE 3. SINGLE-OPERATOR ACCURACY AND PRECISION[a]

Parameter	Average recovery (%)	Standard deviation (%)	Spike range (ug/L)	Number of analyses
Azinphos methyl	72.7	18.8	21-250	17
Bolstar	64.6	6.3	4.9-46	17
Chlorpyrifos	98.3	5.5	1.0-50.5	18
Coumaphos	109.0	12.7	25-225	17
Demeton	67.4	10.5	11.9-314	17
Diazinon	67.0	6.0	5.6	7
Dichlorvos	72.1	7.7	15.6-517	16
Disulfoton	81.9	9.0	5.2-92	17
Ethoprop	100.5	4.1	1.0-51.5	18
Fensulfothion	94.1	17.1	23.9-110	17
Fenthion	68.7	19.9	5.3-64	17
Merphos	120.7	7.9	1.0-50	18
Mevinphos	56.5	7.8	15.5-520	16
Naled	78.0	8.1	25.8-294	16
Parathion methyl	96.0	5.3	0.5-500	21
Phorate	62.7	8.9	4.9-47	17
Ronnel	99.2	5.6	1.0-50	18
Stirophos	66.1	5.9	30.3-505	16
Tokuthion	64.6	6.8	5.3-64	17
Trichloronate	105.0	18.6	20	3

[a]Information taken from Reference 4.


Start
7.1.1 Choose appropriate extraction procedure (see Chapter 2)
7.1.2 Exchange extraction solvent to hexane during K-D procedures
7.2 Set gas chromatography conditions
7.3 Refer to Method 8000 for proper calibration techniques
7.3.2 Is cleanup necessary?
Yes
7.3.2 Process a series of standards through cleanup procedure; analyze by GC
No
A
A
7.4 Perform GC analysis (see Method 8000)
7.4.5 Is identification & detection prevented by interferences ?
Yes
7.5.1 Cleanup using Method 3620 and 3360 if necessary
No
Stop

METHOD 8150

CHLORINATED HERBICIDES

1.0 SCOPE AND APPLICATION

1.1 Method 8150 is a gas chromatographic (GC) method for determining certain chlorinated acid herbicides. Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

1.2 When Method 8150 is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Section 8.4 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.3 Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (the compound is explosive and carcinogenic).

2.0 SUMMARY OF METHOD

2.1 Method 8150 provides extraction, esterification, and gas chromatographic conditions for the analysis of chlorinated acid herbicides. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. The esters are hydrolyzed with potassium hydroxide, and extraneous organic material is removed by a solvent wash. After acidification, the acids are extracted with solvent and converted to their methyl esters using diazomethane as the derivatizing agent. After excess reagent is removed, the esters are determined by gas chromatography employing an electron capture detector, microcoulometric detector, or electrolytic conductivity detector (Goerlitz and Lamar, 1967). The results are reported as the acid equivalents.

2.2 The sensitivity of Method 8150 usually depends on the level of interferences rather than on instrumental limitations.

3.0 INTERFERENCES

3.1 Refer to Method 8000.

3.2 Organic acids, especially chlorinated acids, cause the most direct interference with the determination. Phenols, including chlorophenols, may also interfere with this procedure.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS FOR CHLORINATED HERBICIDES

Compound	Retention time (min)[a]				Method detection limit (ug/L)
	Col.1a	Col.1b	Col.2	Col.3	
2,4-D	2.0	-	1.6	-	1.2
2,4-DB	4.1	-	-	-	0.91
2,4,5-T	3.4	-	2.4	-	0.20
2,4,5-TP (Silvex)	2.7	-	2.0	-	0.17
Dalapon	-	-	-	5.0	5.8
Dicamba	1.2	-	1.0	-	0.27
Dichloroprop	-	4.8	-	-	0.65
Dinoseb	-	11.2	-	-	0.07
MCPA	-	4.1	-	-	249
MCPP	-	3.4	-	-	192

[a]Column conditions are given in Sections 4.1 and 7.4.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

3.3 Alkaline hydrolysis and subsequent extraction of the basic solution remove many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

3.4 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware and glass wool must be acid-rinsed, and sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.1 **Columns:**

4.1.1.1 Column 1a and 1b: 1.8-m x 4-mm I.D. glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent.

4.1.1.2 Column 2: 1.8-m x 4-mm I.D. glass, packed with 5% OV-210 on Gas Chrom Q (100/120 mesh) or equivalent.

4.1.1.3 Column 3: 1.98-m x 2-mm I.D. glass, packed with 0.1% SP-1000 on 80/100 mesh Carbopack C or equivalent.

4.1.2 **Detector:** Electron capture (ECD).

4.2 Erlenmeyer flasks: 250- and 500-mL Pyrex, with 24/40 ground-glass joint.

4.3 Beaker: 500-mL.

4.4 Diazomethane generator: Refer to Section 7.3 to determine which method of diazomethane generation should be used for a particular application.

4.4.1 **Diazald kit:** recommended for the generation of diazomethane using the procedure given in Section 7.3.2 (Aldrich Chemical Co., Cat. No. 210,025-2 or equivalent).

4.4.2 Assemble from two 20 x 150-mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen. Use Neoprene rubber stoppers with holes drilled in them to accommodate glass delivery tubes. The exit tube must be drawn to a point to bubble diazomethane through the sample extract. The generator assembly is shown in Figure 1. The procedure for use of this type of generator is given in Section 7.3.3.

4.5 Vials: Amber glass, 10- to 15-mL capacity with Teflon-lined screw cap.

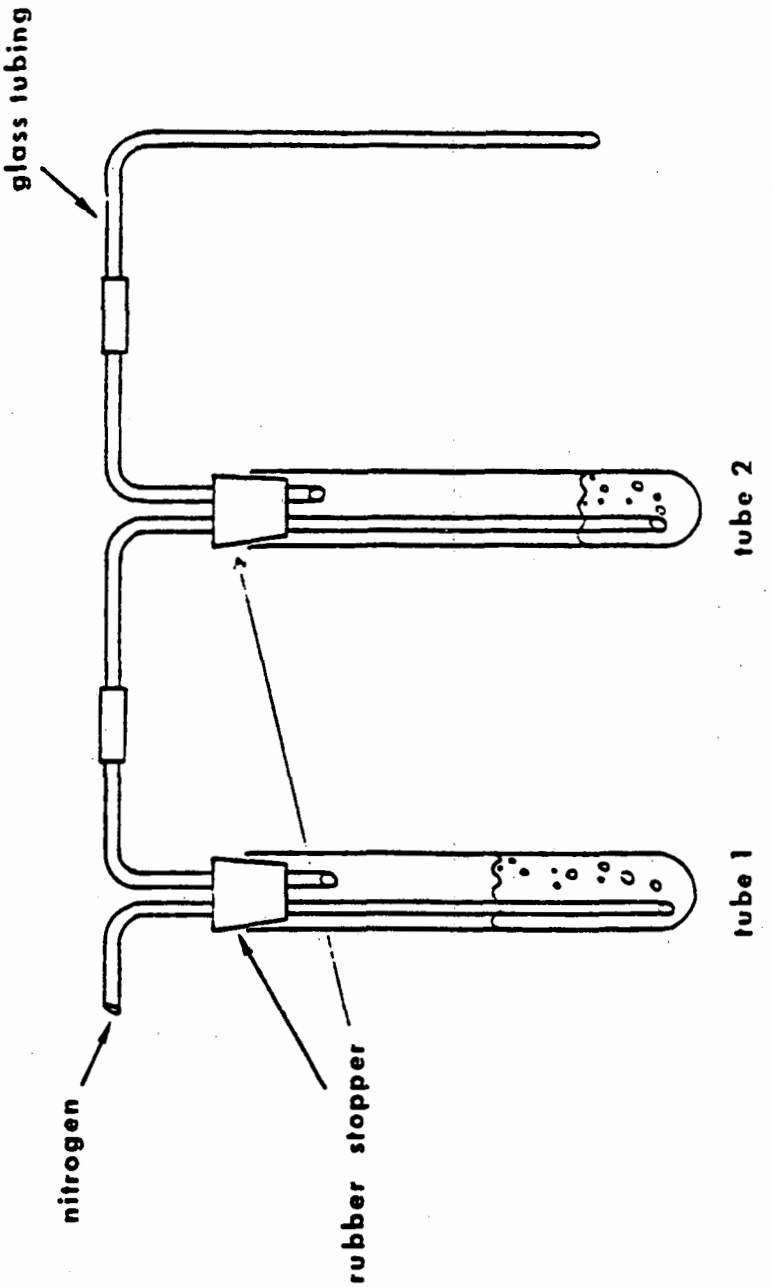


Figure 1. Diazomethane generator.

4.6 Separatory funnel: 2-L, 125-mL, and 60-mL.

4.7 Drying column: 400-mm x 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.
NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.8 Kuderna-Danish (K-D) apparatus:

4.8.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts

4.8.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.8.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.8.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.9 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.10 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.11 Microsyringe: 10-uL.

4.12 Wrist shaker: Burrell Model 75 or equivalent.

4.13 Glass wool: Pyrex, acid washed.

4.14 Balance: Analytical, capable of accurately weighting to the nearest 0.0001 g.

4.15 Syringe: 5-mL.

4.16 Glass rod.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.

5.2 Sulfuric acid solution:

5.2.1 (1:1) (v/v) - slowly add 50 mL H_2So_4 (sp. gr. 1.84) to 50 mL of reagent water.

5.2.2 (1:3) (v/v) - slowly add 25 mL H_2So_4 (sp. gr. 1.84) to 75 mL of reagent water.

5.3 Hydrochloric acid: (ACS), (1:9) (v/v) - add one volume of concentrated HCl to 9 volumes of reagent water.

5.4 Potassium hydroxide solution: 37% aqueous solution (w/v). Dissolve 37 g ACS grade potassium hydroxide pellets in reagent water and dilute to 100 mL.

5.5 Carbitol (Diethylene glycol monoethyl ether): (ACS), available from Aldrich Chemical Co.

5.6 Solvents:

5.6.1 Acetone, methanol, ethanol, methylene chloride, hexane (pesticide quality or equivalent).

5.6.2 **Diethyl ether:** Pesticide quality or equivalent. Must be free of peroxides, as indicated by EM Quant test strips (available from Scientific Products Co., Cat. No. P1126-8, and other suppliers). Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL ethanol preservative must be added to each liter of ether.

5.7 Sodium sulfate: (ACS) granular, acidified, anhydrous. Heat treat in a shallow tray at 400°C for a minimum of 4 hr to remove phthalates and other interfering organic substances. Alternatively, heat 16 hr at 400-500°C in a shallow tray or Soxhlet extract with methylene chloride for 48 hr. Acidify by slurrying 100 g sodium sulfate with enough diethyl ether to just cover the solid; then add 0.1 mL of concentrated sulfuric acid and mix thoroughly. Remove the ether under a vacuum. Mix 1 g of the resulting solid with 5 mL of reagent water and measure the pH of the mixture. It must be below a pH of 4. Store at 130°C.

5.8 N-Methyl-N-nitroso-p-toluenesulfonamide (Diazald): (ACS) available from Aldrich Chemical Co.

5.9 Silicic acid: chromatographic grade, nominal 100 mesh. Store at 130°C.

5.10 Stock standard solutions: Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.10.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure acids. Dissolve the material in pesticide quality diethyl ether and dilute to volume in a 10-mL volumetric flask. Larger

volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commerically prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.10.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.10.3 Stock standard solutions must be replaced after 1 year, or sooner if comparison with check standards indicates a problem.

5.11 Calibration standards: Calibration standards at a minimum of five concentration levels for each parameter of interest should be prepared through dilution of the stock standards with diethyl ether. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.12 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.12.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Paragraph 5.11.

5.12.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with diethyl ether.

5.12.3 Analyze each calibration standard according to Section 7.0.

5.13 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two herbicide surrogates (e.g., herbicides that are not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Preparation of solid samples:

7.1.1 **Extraction:**

7.1.1.1 To a 500-mL, wide-mouth Erlenmeyer flask add 50 g (dry weight) of the well-mixed, moist solid sample. Adjust the pH to 2 with concentrated HCl and monitor the pH for 15 min with occasional stirring. If necessary, add additional HCl until the pH remains at 2.

7.1.1.2 Add 20 mL acetone to the flask and mix the contents with the wrist shaker for 20 min. Add 80 mL diethyl ether to the same flask and shake again for 20 min. Decant the extract and measure the volume of solvent recovered.

7.1.1.3 Extract the sample twice more using 20 mL of acetone followed by 80 mL of diethyl ether. After addition of each solvent, the mixture should be shaken with the wrist shaker for 10 min and the acetone-ether extract decanted.

7.1.1.4 After the third extraction, the volume of extract recovered should be at least 75% of the volume of added solvent. If this is not the case, additional extractions may be necessary. Combine the extracts in a 2-liter separatory funnel containing 250 mL of 5% acidified sodium sulfate. If an emulsion forms, slowly add 5 g of acidified sodium sulfate (anhydrous) until the solvent-water mixture separates. A quantity of acidified sodium sulfate equal to the weight of the sample may be added, if necessary.

7.1.1.5 Check the pH of the extract. If it is not at or below pH 2, add more concentrated HCl until stabilized at the desired pH. Gently mix the contents of the separatory funnel for 1 min and allow the layers to separate. Collect the aqueous phase in a clean beaker and the extract phase (top layer) in a 500-mL ground-glass Erlenmeyer flask. Place the aqueous phase back into the separatory funnel and re-extract using 25 mL of diethyl ether. Allow the layers to separate and discard the aqueous layer. Combine the ether extracts in the 500-mL Erlenmeyer flask.

7.1.2 **Hydrolysis:**

7.1.2.1 Add 30 mL of reagent water, 5 mL of 37% KOH, and one or two clean boiling chips to the flask. Place a three-ball Snyder column on the flask, evaporate the diethyl ether on a water bath, and continue to heat for a total of 90 min.

7.1.2.2 Remove the flask from the water bath and allow to cool. Transfer the water solution to a 125-mL separatory funnel and extract the basic solutions once with 40 mL and then twice with 20 mL of diethyl ether. Allow sufficient time for the layers to separate and discard the ether layer each time. The phenoxy acid herbicides remain soluble in the aqueous phase as potassium salts.

7.1.3 **Solvent cleanup:**

7.1.3.1 Adjust the pH to 2 by adding 5 mL cold (4°C) sulfuric acid (1:3) to the separatory funnel. Be sure to check the pH at this point. Extract the herbicides once with 40 mL and twice with 20 mL of diethyl ether. Discard the aqueous phase.

7.1.3.2 Combine ether extracts in a 125-mL Erlenmeyer flask containing 1.0 g of acidified anhydrous sodium sulfate. Stopper and allow the extract to remain in contact with the acidified sodium sulfate. If concentration and esterification are not to be performed immediately, store the sample overnight in the refrigerator.

7.1.3.3 Transfer the ether extract, through a funnel plugged with acid-washed glass wool, into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer.

7.1.3.4 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

7.1.3.5 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. A 5-mL syringe is recommended for this operation. Add a fresh boiling chip, attach a micro-Snyder column to the concentrator tube, and prewet the column by adding 0.5 mL of ethyl ether to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5-10 min. When the apparent volume of the liquid reaches 0.5 mL, remove the micro-K-D from the

bath and allow it to drain and cool. Remove the Snyder column and add 0.1 mL of methanol. Rinse the walls of the concentrator tube while adjusting the extract volume to 1.0 mL with diethyl ether. Proceed to Section 7.3 for esterification.

7.2 Preparation of liquid samples:

7.2.1 Extraction:

7.2.1.1 Mark the water miniscus on the side of the sample container for later determination of sample volume. Pour the entire sample into a 2-liter separatory funnel and check the pH with wide-range pH paper. Adjust the pH to less than 2 with sulfuric acid (1:1).

7.2.1.2 Add 150 mL of diethyl ether to the sample bottle, seal, and shake for 30 sec to rinse the walls. Transfer the solvent wash to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water layer for a minimum of 10 min. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Drain the aqueous phase into a 1-liter Erlenmeyer flask. Collect the solvent extract in a 250-mL ground-glass Erlenmeyer flask containing 2 mL of 37% KOH. Approximately 80 mL of the diethyl ether will remain dissolved in the aqueous phase.

7.2.1.3 Repeat the extraction two more times using 50 mL of diethyl ether each time. Combine the extracts in the Erlenmeyer flask. (Rinse the 1-liter flask with each additional aliquot of extracting solvent.)

7.2.2 Hydrolysis:

7.2.2.1 Add one or two clean boiling chips and 15 mL of reagent water to the 250-mL flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top of the column. Place the apparatus on a hot water bath (60°-65°C) so that the bottom of the flask is bathed with hot water vapor. Although the diethyl ether will evaporate in about 15 min, continue heating for a total of 60 min, beginning from the time the flask is placed in the water bath. Remove the apparatus and let stand at room temperature for at least 10 min.

7.2.2.2 Transfer the solution to a 60-mL separatory funnel using 5-10 mL of reagent water. Wash the basic solution twice by shaking for 1 min with 20-mL portions of diethyl ether. Discard the organic phase. The herbicides remain in the aqueous phase.

7.2.3 **Solvent cleanup:**

7.2.3.1 Acidify the contents of the separatory funnel to pH 2 by adding 2 mL of cold (4°C) sulfuric acid (1:3). Test with pH indicator paper. Add 20 mL diethyl ether and shake vigorously for 2 min. Drain the aqueous layer into a 250-mL Erlenmeyer flask, and pour the organic layer into a 125-mL Erlenmeyer flask containing about 0.5 g of acidified sodium sulfate. Repeat the extraction twice more with 10-mL aliquots of diethyl ether, combining all solvent in the 125-mL flask. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hr.

7.2.3.2 Transfer the ether extract, through a funnel plugged with acid-washed glass wool, into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer.

7.2.3.3 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

7.2.3.4 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. A 5-mL syringe is recommended for this operation. Add a fresh boiling chip, attach a micro-Snyder column to the concentrator tube, and prewet the column by adding 0.5 mL of ethyl ether to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5-10 min. When the apparent volume of the liquid reaches 0.5 mL, remove the micro-K-D from the bath and allow it to drain and cool. Remove the Snyder column and add 0.1 mL of methanol. Rinse the walls of the concentrator tube while adjusting the extract volume to 1.0 mL with diethyl ether.

7.2.3.5 Determine the original sample volume by refilling the sample bottle to the mark with water and transferring to a 1-liter graduated cylinder. Record the sample volume to the nearest 5 mL.

7.3 Esterification:

7.3.1 Two methods may be used for the generation of diazomethane: the bubbler method (set up shown in Figure 1) and the Diazald kit method. The bubbler method is suggested when small batches (10-15) of samples require esterification. The bubbler method works well with samples that have low concentrations of herbicides (e.g., aqueous samples) and is safer to use than the Diazald kit procedure. The Diazald kit method is good for large quantities of samples needing esterification. The Diazald kit method is more effective than the bubbler method for soils or samples that may contain high concentrations of herbicides (e.g., samples such as soils that may result in yellow extracts following hydrolysis may be difficult to handle by the bubbler method). The diazomethane derivatization (U.S. EPA, 1971) procedures, described below, will react efficiently with all of the chlorinated herbicides described in this method and should be used only by experienced analysts, due to the potential hazards associated with its use. The following precautions should be taken:

CAUTION: Diazomethane is a carcinogen and can explode under certain conditions.

- Use a safety screen.
- Use mechanical pipetting aides.
- Do not heat above 90°C -- EXPLOSION may result.
- Avoid grinding surfaces, ground-glass joints, sleeve bearings, glass stirrers -- EXPLOSION may result.
- Store away from alkali metals -- EXPLOSION may result.
- Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

7.3.2 **Diazald kit method:** Instructions for preparing diazomethane are provided with the generator kit.

7.3.2.1 Add 2 mL of diazomethane solution and let sample stand for 10 min with occasional swirling.

7.3.2.2 Rinse inside wall of ampule with several hundred uL of diethyl ether. Allow solvent to evaporate spontaneously at room temperature to about 2 mL.

7.3.2.3 Dissolve the residue in 5 mL of hexane. Analyze by gas chromatography.

7.3.3 **Bubbler method:** Assemble the diazomethane bubbler (see Figure 1).

7.3.3.1 Add 5 mL of diethyl ether to the first test tube. Add 1 mL of diethyl ether, 1 mL of carbitol, 1.5 mL of 37% KOH, and 0.1-0.2 g Diazald to the second test tube. Immediately place the exit tube into the concentrator tube containing the sample extract.

Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 10 min or until the yellow color of diazomethane persists. The amount of Diazald used is sufficient for esterification of approximately three sample extracts. An additional 0.1-0.2 g of Diazald may be added (after the initial Diazald is consumed) to extend the generation of the diazomethane. There is sufficient KOH present in the original solution to perform a maximum of approximately 20 min of total esterification.

7.3.3.2 Remove the concentrator tube and seal it with a Neoprene or Teflon stopper. Store at room temperature in a hood for 20 min.

7.3.3.3 Destroy any unreacted diazomethane by adding 0.1-0.2 g silicic acid to the concentrator tube. Allow to stand until the evolution of nitrogen gas has stopped. Adjust the sample volume to 10.0 mL with hexane. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. It is recommended that the methylated extracts be analyzed immediately to minimize the trans-esterification and other potential reactions that may occur. Analyze by gas chromatography.

7.4 Gas chromatography conditions (Recommended):

7.4.1 **Column 1a:** Set 5% methane/95% argon carrier gas flow at 70-mL/min flow rate. Column temperature is set at 185°C isothermal.

7.4.2 **Column 1b:** Set 5% methane/95% argon carrier gas flow at 70-mL/min flow rate. Column temperature is set at 140°C for 6 min and then programmed at 10°C/min to 200°C and held.

7.4.3 **Column 2:** Set 5% methane/95% argon carrier gas at 70-mL/min flow rate. Column temperature is set at 185°C isothermal.

7.4.4 **Column 3:** Set nitrogen (ultra-high purity) carrier gas at 25-mL/min flow rate. Column temperature is set at 100°C and then immediately programmed at 10°C/min to 150°C and held.

7.5 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.5.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.5.2 The following gas chromatographic columns are recommended for the compounds indicated:

Parameter	Column
Dicamba	1a,2
2,4-D	1a,2
2,4,5-TP	1a,2
2,4,5-T	1a,2
2,4-DB	1a
Dalapon	3
MCPP	1b
MCPA	1b
Dichloroprop	1b
Dinoseb	1b

7.6 Gas chromatographic analysis:

7.6.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.6.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.6.3 Examples of chromatograms for various chlorophenoxy herbicides are shown in Figures 2 through 4.

7.6.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.6.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.6.6 If calibration standards have been analyzed in the same manner as the samples (e.g., have undergone hydrolysis and esterification), then the calculation of concentration given in Method 8000, Section 7.8 should be used. However, if calibration is done using standards made from methyl ester compounds (compounds not esterified by application of this method), then the calculation of concentration must include a correction for the molecular weight of the methyl ester versus the acid herbicide.

7.6.7 If peak detection and identification are prevented due to interferences, further cleanup is required. Before using any cleanup procedure, the analyst must process a series of standards through the procedure to validate elution patterns and the absence of interferences from reagents.

Column: 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 Mesh)
Temperature: Isothermal at 185°C
Detector: Electron Capture

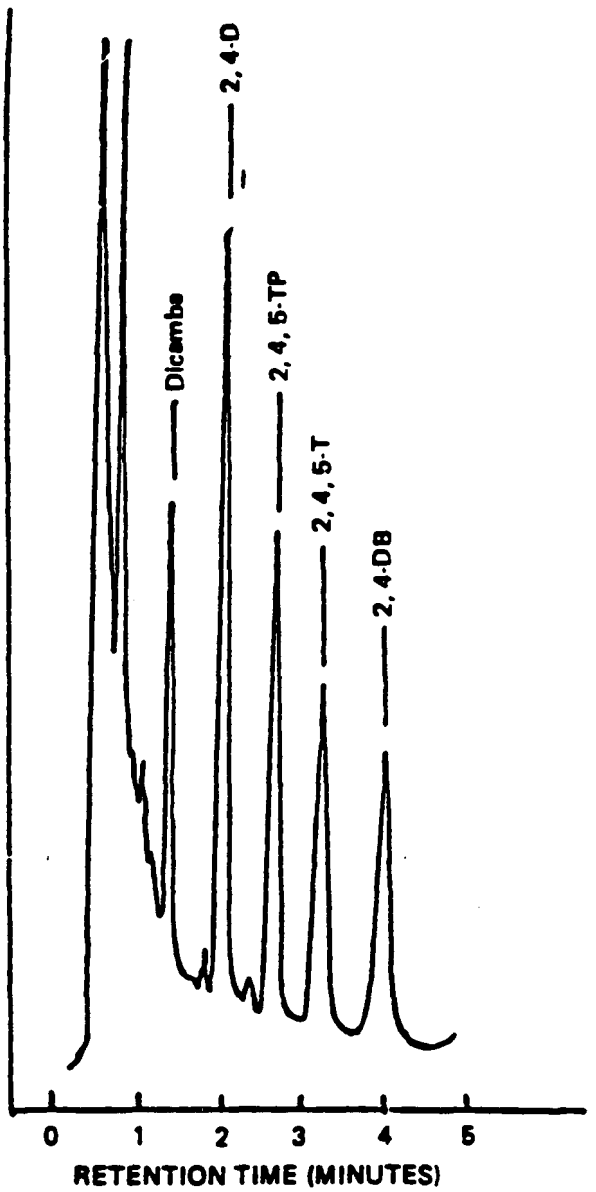


Figure 2. Gas chomatogram of chlorinated herbicides.

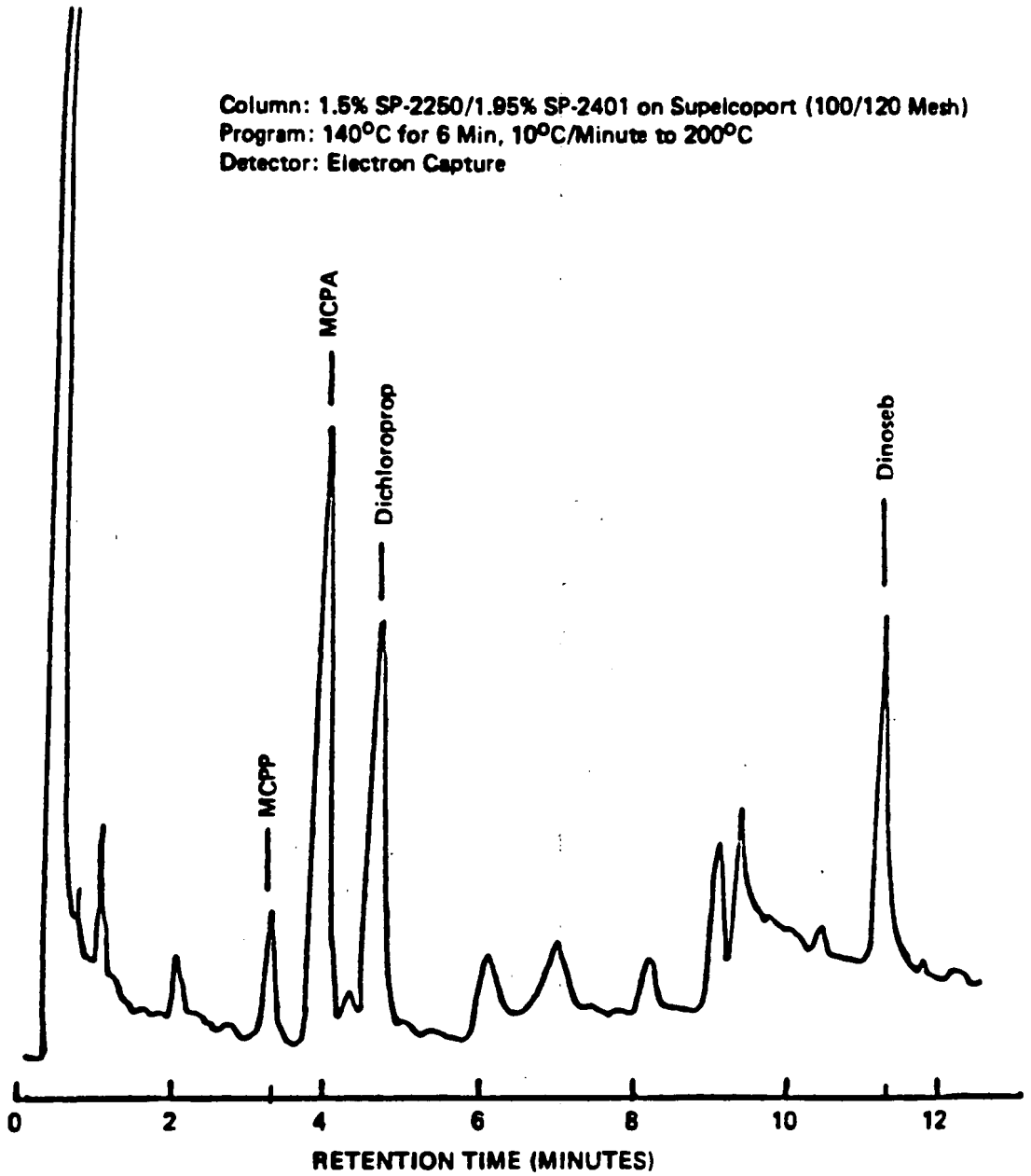


Figure 3. Gas chromatogram of chlorinated herbicides.

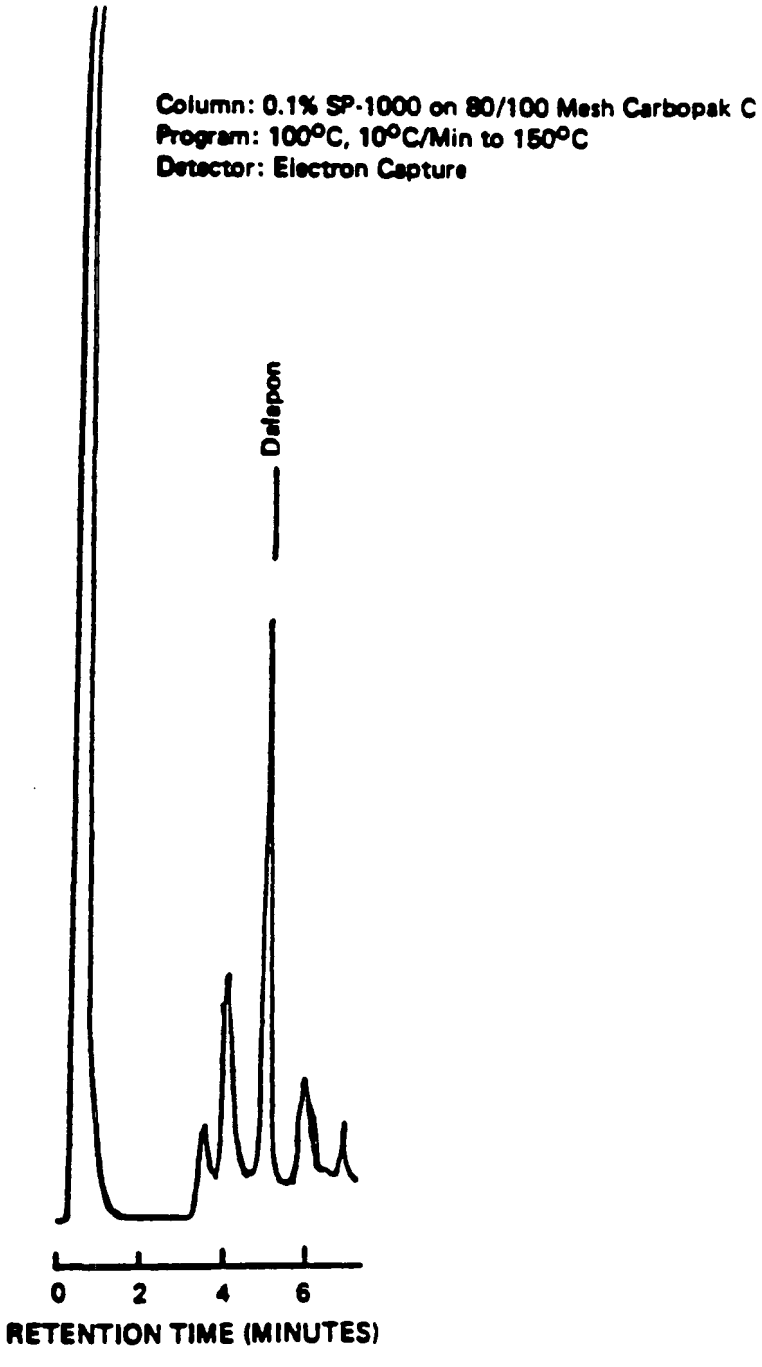


Figure 4. Gas chromatogram of dalapon, column 3.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

8.2.1 Select a representative spike concentration for each compound (acid or ester) to be measured. Using stock standards, prepare a quality control check sample concentrate in acetone 1,000 times more concentrated than the selected concentrations.

8.2.2 Table 3 indicates Single Operator Accuracy and Precision for this method. Compare the results obtained with the results given in Table 3 to determine if the data quality is acceptable.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.4 GC/MS confirmation:

8.4.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Refer to Method 8270 for the appropriate GC/MS operating conditions and analysis procedures.

8.4.2 When available, chemical ionization mass spectra may be employed to aid the qualitative identification process.

8.4.3 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns or additional cleanup.

9.0 METHOD PERFORMANCE

9.1 In a single laboratory, using reagent water and effluents from publicly owned treatment works (POTW), the average recoveries presented in Table 3 were obtained. The standard deviations of the percent recoveries of these measurements are also included in Table 3.

10.0 REFERENCES

1. U.S. EPA, National Pollutant Discharge Elimination System, Appendix A, Fed. Reg., 38, No. 75, Pt. II, Method for Chlorinated Phenoxy Acid Herbicides in Industrial Effluents, Cincinnati, Ohio, 1971.

2. Goerlitz, D.G., and W.L. Lamar, "Determination of Phenoxy Acid Herbicides in Water by Electron Capture and Microcoulometric Gas Chromatography," U.S. Geol. Survey Water Supply Paper, 1817-C, 1967.

3. Burke, J.A., "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

4. U.S. EPA, "Extraction and Cleanup Procedure for the Determination of Phenoxy Acid Herbicides in Sediment," EPA Toxicant and Analysis Center, Bay St. Louis, Mississippi, 1972.

5. "Pesticide Methods Evaluation," Letter Report #33 for EPA Contract No. 68-03-2697. Available from U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

6. McNair, H.M. and E.J. Bonelli, "Basic Chromatography," Consolidated Printing, Berkeley, California, p. 52, 1969.

7. Eichelberger, J.W., L.E. Harris, and W.L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry," Analytical Chemistry, 47, 995, 1975.

8. Glaser, J.A. et.al., "Trace Analysis for Wastewaters," Environmental Science & Technology, 15, 1426, 1981.

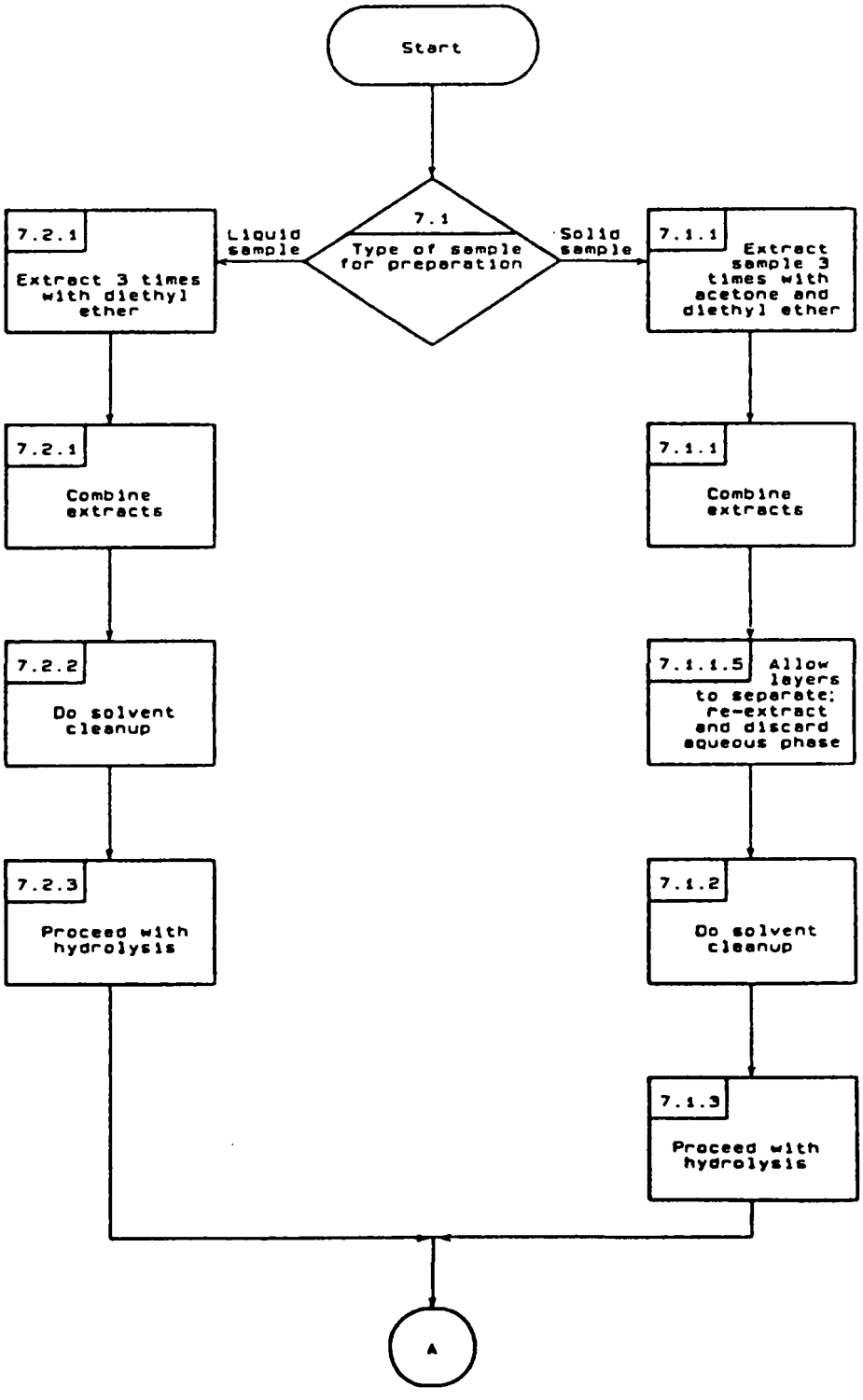
9. U.S. EPA, "Method 615. The Determination of Chlorinated Herbicides in Industrial and Municipal Wastewater," Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268, June 1982.

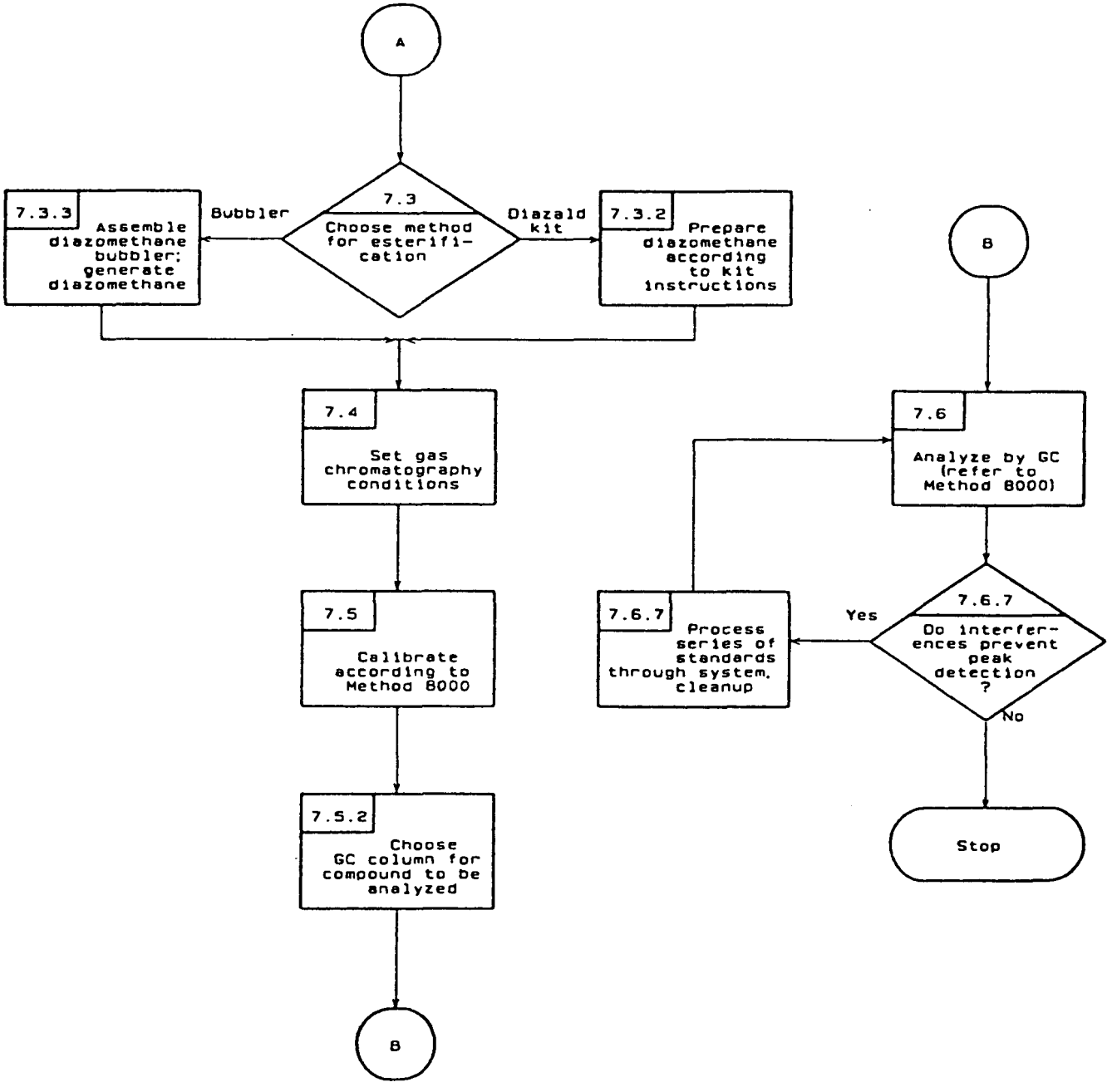
TABLE 3. SINGLE-OPERATOR ACCURACY AND PRECISION[a]

Parameter	Sample Type	Spike (ug/L)	Mean Recovery (%)	Standard deviation (%)
2,4-D	DW	10.9	75	4
	MW	10.1	77	4
	MW	200	65	5
Dalapon	DW	23.4	66	8
	MW	23.4	96	13
	MW	468	81	9
2,4-DB	DW	10.3	93	3
	MW	10.4	93	3
	MW	208	77	6
Dicamba	DW	1.2	79	7
	MW	1.1	86	9
	MW	22.2	82	6
Dichlorprop	DW	10.7	97	2
	MW	10.7	72	3
	MW	213	100	2
Dinoseb	MW	0.5	86	4
	MW	102	81	3
MCPA	DW	2020	98	4
	MW	2020	73	3
	MW	21400	97	2
MCPP	DW	2080	94	4
	MW	2100	97	3
	MW	20440	95	2
2,4,5-T	DW	1.1	85	6
	MW	1.3	83	4
	MW	25.5	78	5
2,4,5-TP	DW	1.0	88	5
	MW	1.3	88	4
	MW	25.0	72	5

[a]All results based upon seven replicate analyses. Esterification performed using the bubbler method. Data obtained from reference 9.

DW = Reagent water
MW = Municipal water


Start
7.1
Type of sample for preparation
Liquid sample
Solid sample
7.2.1
Extract 3 times with diethyl ether
7.1.1
Extract sample 3 times with acetone and diethyl ether
7.2.1
Combine extracts
7.1.1
Combine extracts
7.2.2
Do solvent cleanup
7.1.1.5
Allow layers to separate; re-extract and discard aqueous phase
7.2.3
Proceed with hydrolysis
7.1.2
Do solvent cleanup
7.1.3
Proceed with hydrolysis
A


A
7.3
Choose method for esterification
Bubbler
Diazald kit
7.3.3
Assemble diazomethane bubbler; generate diazomethane
7.3.2
Prepare diazomethane according to kit instructions
7.4
Set gas chromatography conditions
7.5
Calibrate according to Method 8000
7.5.2
Choose GC column for compound to be analyzed
B
B
7.6
Analyze by GC (refer to Method 8000)
7.6.7
Do interferences prevent peak detection ?
Yes
No
7.6.7
Process series of standards through system, cleanup
Stop

METHOD 8240

GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR VOLATILE ORGANICS

1.0 SCOPE AND APPLICATION

1.1 Method 8240 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.2 Method 8240 can be used to quantify most volatile organic compounds that have boiling points below 200°C [vapor pressure is approximately equal to mm Hg @ 25°C] and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique, however, for the more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax. Such compounds include low-molecular-weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Table 1 for a list of compounds, retention times, and their characteristic ions that have been evaluated on a purge-and-trap GC/MS system.

1.3 The practical quantitation limit (PQL) of Method 8240 for an individual compound is approximately 5 ug/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 ug/L for ground water (see Table 2). PQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

1.4 Method 8240 is based upon a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. This method is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

1.5 To increase purging efficiencies of acrylonitrile and acrolein, refer to Methods 5030 and 8030 for proper purge-and-trap conditions.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by direct injection (in limited applications). The components are separated via the gas chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information. The chromatographic conditions, as well as typical mass spectrometer operating parameters, are given.

TABLE 1. RETENTION TIMES AND CHARACTERISTIC IONS FOR VOLATILE COMPOUNDS

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Acetone	--	43	58
Acrolein	--	56	55, 58
Acrylonitrile	--	53	52, 51
Benzene	17.0	78	52, 77
Bromochloromethane (I.S.)	9.3	128	49, 130, 51
Bromodichloromethane	14.3	83	85, 129
4-Bromofluorobenzene (surr.)	28.3	95	174, 176
Bromoform	19.8	173	171, 175, 252
Bromomethane	3.1	94	96, 79
2-Butanone	--	72	57, 43
Carbon disulfide	--	76	78
Carbon tetrachloride	13.7	117	119, 121
Chlorobenzene	24.6	112	114, 77
Chlorobenzene-d_5 (I.S.)	--	117	82, 119
Chlorodibromomethane	--	129	208, 206
Chloroethane	4.6	64	66, 49
2-Chloroethyl vinyl ether	18.6	63	65, 106
Chloroform	11.4	83	85, 47
Chloromethane	2.3	50	52, 49
Dibromomethane	--	93	174, 95
1,4-Dichloro-2-butane	--	75	53, 89
Dichlorodifluoromethane	--	85	87, 50, 101
1,1-Dichloroethane	--	63	65, 83
1,2-Dichloroethane	10.1	62	64, 98
1,2-Dichloroethane-d_4 (surr.)	12.1	65	102
1,1-Dichloroethene	9.0	96	61, 98
trans-1,2-Dichloroethene	10.0	96	61, 98
1,2-Dichloropropane	15.7	63	62, 41
cis-1,3-Dichloropropene	15.9	75	77, 39
trans-1,3-Dichloropropene	17.2	75	77, 39
1,4-Difluorobenzene (I.S.)	19.6	114	63, 88
Ethanol	--	31	45, 27, 46
Ethylbenzene	26.4	106	91
Ethyl methacrylate	--	69	41, 39, 99
2-Hexanone	--	43	58, 57, 100
Iodomethane	--	142	127, 141
Methylene chloride	6.4	84	49, 51, 86
4-Methyl-2-pentanone	--	43	58, 100
Styrene	--	104	78, 103
1,1,2,2-Tetrachloroethane	22.1	83	85, 131, 133
Tetrachloroethene	22.2	164	129, 131, 166
Toluene	23.5	92	91, 65
Toluene-d_8 (surr.)	--	98	70, 100

TABLE 1. - Continued

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
1,1,1-Trichloroethane	13.4	97	99, 117
1,1,2-Trichloroethane	17.2	97	83, 85, 99
Trichloroethene	16.5	130	95, 97, 132
Trichlorofluoromethane	8.3	101	103, 66
1,2,3-Trichloropropane	--	75	110, 77, 61
Vinyl acetate	--	43	86
Vinyl chloride	3.8	62	64, 61
Xylene	--	106	91

TABLE 2. PRACTICAL QUANTITATION LIMITS (PQL) FOR VOLATILE ORGANICS[a]

Volatiles	CAS Number	Practical Quantitation Limits[b] Ground water ug/L	Low Soil/Sediment ug/Kg
1. Chloromethane	74-87-3	10	10
2. Bromomethane	74-83-9	10	10
3. Vinyl Chloride	75-01-4	10	10
4. Chloroethane	75-00-3	10	10
5. Methylene Chloride	75-09-2	5	5
6. Acetone	67-64-1	100	100
7. Carbon Disulfide	75-15-0	5	5
8. 1,1-Dichloroethene	75-35-4	5	5
9. 1,1-Dichloroethane	75-35-3	5	5
10. trans-1,2-Dichloroethene	156-60-5	5	5
11. Chloroform	67-66-3	5	5
12. 1,2-Dichloroethane	107-06-2	5	5
13. 2-Butanone	78-93-3	100	100
14. 1,1,1-Trichloroethane	71-55-6	5	5
15. Carbon Tetrachloride	56-23-5	5	5
16. Vinyl Acetate	108-05-4	50	50
17. Bromodichloromethane	75-27-4	5	5
18. 1,1,2,2-Tetrachloroethane	79-34-5	5	5
19. 1,2-Dichloropropane	78-87-5	5	5
20. trans-1,3-Dichloropropene	10061-02-6	5	5
21. Trichloroethene	79-01-6	5	5
22. Dibromochloromethane	124-48-1	5	5
23. 1,1,2-Trichloroethane	79-00-5	5	5
24. Benzene	71-43-2	5	5
25. cis-1,3-Dichloropropene	10061-01-5	5	5
26. 2-Chloroethyl Vinyl Ether	110-75-8	10	10
27. Bromoform	75-25-2	5	5
28. 2-Hexanone	591-78-6	50	50
29. 4-Methyl-2-pentanone	108-10-1	50	50
30. Tetrachloroethene	127-18-4	5	5

TABLE 2. - Continued

Volatiles	CAS Number	Practical Quantitation Limits[b] Ground water ug/L	Low Soil/Sediment ug/Kg
31. Toluene	108-88-3	5	5
32. Chlorobenzene	108-90-7	5	5
33. Ethyl Benzene	100-41-4	5	5
34. Styrene	100-42-5	5	5
35. Total Xylenes		5	5

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achieveable. See the following information for further guidance on matrix-dependent PQLs.

[b]PQLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis; therefore, PQLs will be higher, based on the % moisture in each sample.

Other Matrices:	Factor[1]
Water miscible liquid waste	50
High-level soil & sludges	125
Non-water miscible waste	500

[1]PQL = [PQL for ground water (Table 2)] X [Factor]. For non-aqueous samples, the factor is on a wet-weight basis.

2.2 If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is combined with water in a specially designed purging chamber. It is then analyzed by purge-and-trap GC/MS following the normal water method.

2.3 The purge-and-trap process: An inert gas is bubbled through the solution at ambient temperature, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is heated to elute the components, which are detected with a mass spectrometer.

3.0 INTERFERENCES

3.1 Interferences purged or coextracted from the samples will vary considerably from source to source, depending upon the particular sample or extract being tested. The analytical system, however, should be checked to ensure freedom from interferences, under the analysis conditions, by analyzing method blanks.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of reagent water to check for cross-contamination. The purge-and-trap system may require extensive bake-out and cleaning after a high-level sample.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents.

3.5 Impurities in the purge gas and from organic compounds out-gasing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE plastic coating, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringes: 10-uL, 25-uL, 100-uL, 250-uL, 500-uL, and 1,000 uL. These syringes should be equipped with a 20-gauge (0.006-in I.D.) needle

having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device. The needle length will depend upon the dimensions of the purging device employed.

4.2 Syringe valve: Two-way, with Luer ends (three each), if applicable to the purging device.

4.3 Syringe: 5-mL, gas-tight with shutoff valve.

4.4 Balance: Analytical, capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.1 g.

4.5 Glass scintillation vials: 20-mL, with screw caps and Teflon liners or glass culture tubes with a screw cap and Teflon liner.

4.6 Volumetric flasks: 10-mL and 100-mL, class A with ground-glass stoppers.

4.7 Vials: 2-mL, for GC autosampler.

4.8 Spatula: Stainless steel.

4.9 Disposable pipets: Pasteur.

4.10 Heater or heated oil bath: Should be capable of maintaining the purging chamber to within 1°C over the temperature range of ambient to 100°C.

4.11 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.11.1 The recommended purging chamber is designed to accept 5-mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3-mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria. Alternate sample purge devices may be utilized, provided equivalent performance is demonstrated.

4.11.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap must contain the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap (see Figure 2). If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated

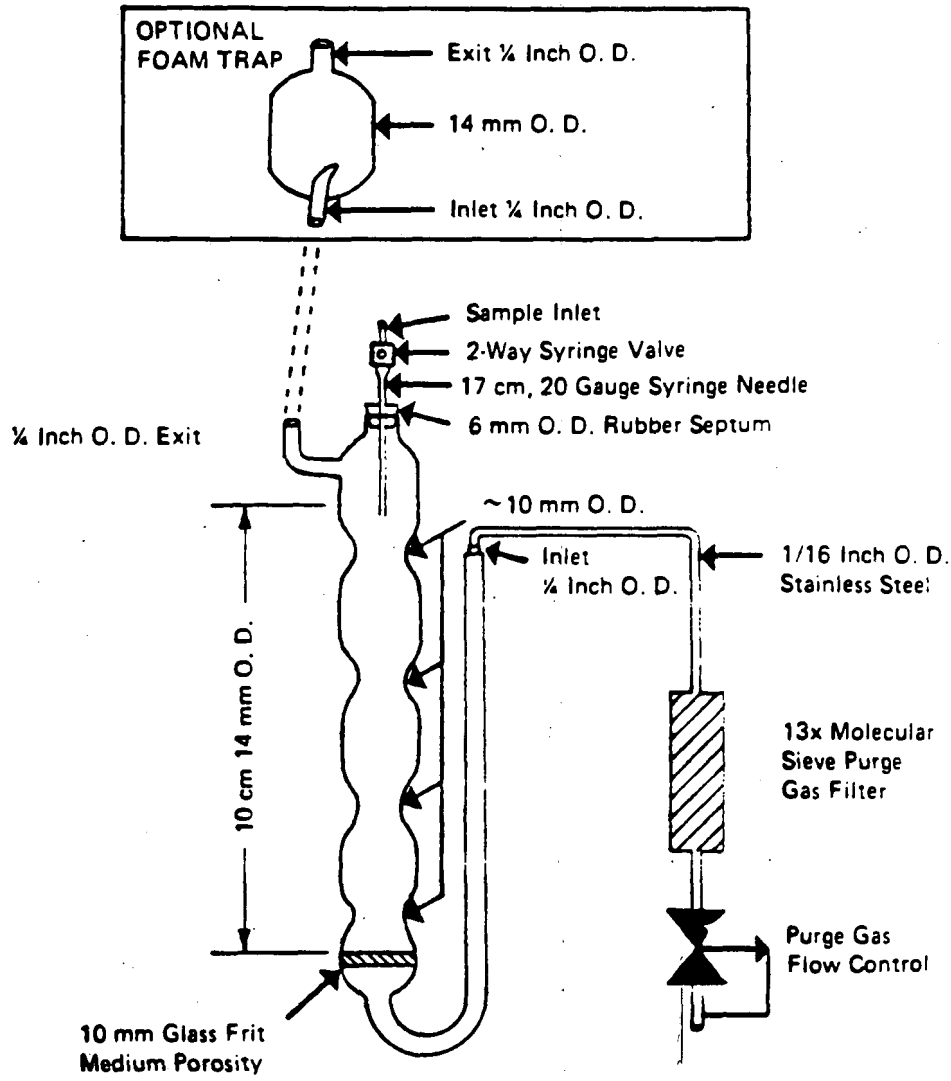


Figure 1. Purging chamber.

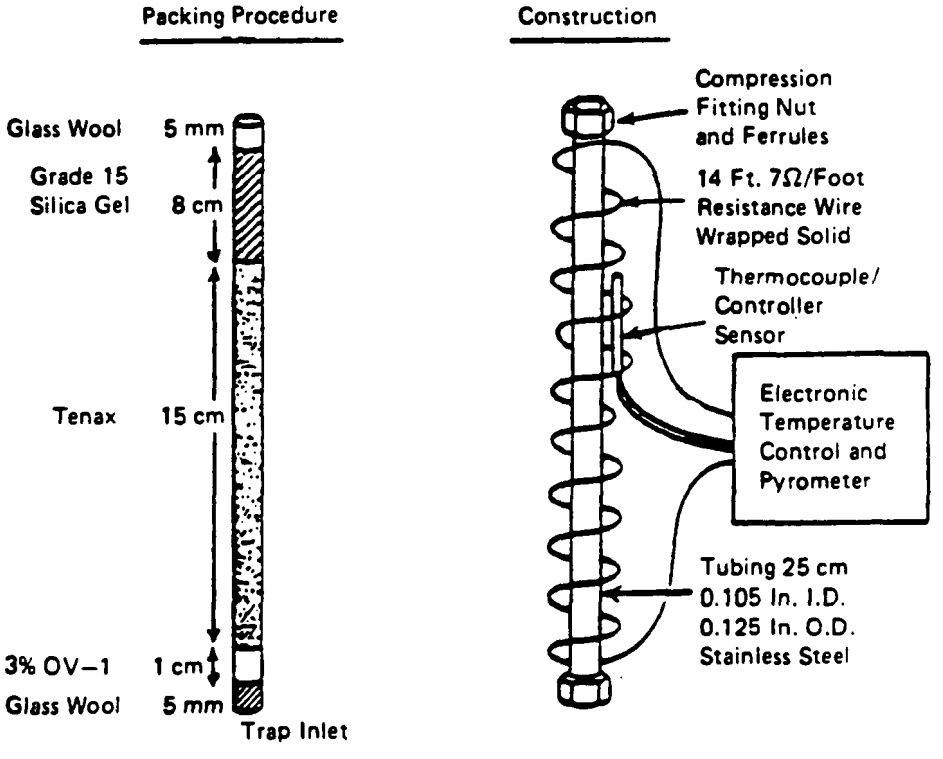


Figure 2. Trap packings and construction to include desorb capability for Method 8240.

and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

4.11.3 The desorber should be capable of rapidly heating the trap to 180°C for desorption. The polymer section of the trap should not be heated higher than 180°C, and the remaining sections should not exceed 220°C during bake-out mode. The desorber design illustrated in Figure 2 meets these criteria.

4.11.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 3 and 4.

4.11.5 **Trap Packing Materials:**

4.11.5.1 2,6-Diphenylene oxide polymer: 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.11.5.2 Methyl silicone packing: OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.11.5.3 Silica gel: 35/60 mesh, Davison, grade 15 or equivalent.

4.11.5.4 Coconut charcoal: Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 by crushing through 26 mesh screen.

4.12 Gas chromatograph/mass spectrometer system:

4.12.1 **Gas chromatograph:** An analytical system complete with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.12.2 **Column:** 6-ft x 0.1-in. I.D. glass, packed with 1% SP-1000 on Carbopack-B (60/80 mesh) or equivalent.

4.12.3 **Mass spectrometer:** Capable of scanning from 35-260 amu every 3 sec or less, using 70 volts (nominal) electron energy in the electron impact mode and producing a mass spectrum that meets all the criteria in Table 3 when 50 ng of 4-bromofluorobenzene (BFB) are injected through the gas chromatograph inlet.

4.12.4 **GC/MS interface:** Any GC-to-MS interface that gives acceptable calibration points at 50 ng or less per injection for each of the analytes and achieves all acceptable performance criteria (see Table 3) may be used. GC-to-MS interfaces constructed entirely of glass or of

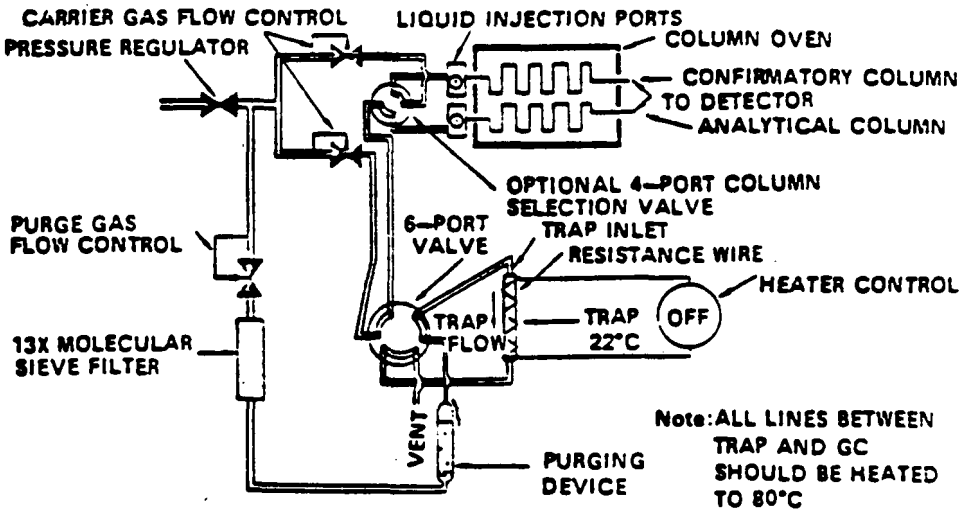


Figure 3. Schematic of purge-and-trap device – purge mode for Method 8240.

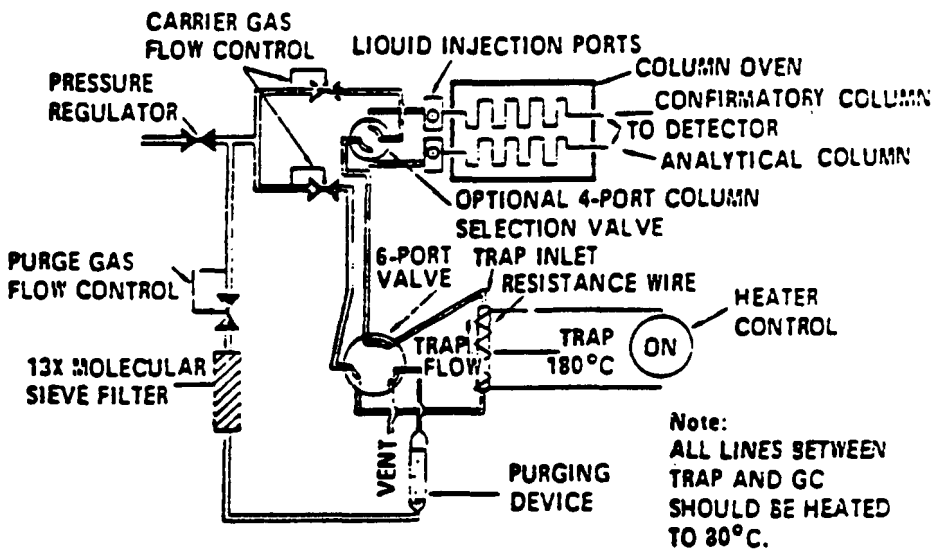


Figure 4. Schematic of purge-and-trap device – desorb mode for Method 8240.

TABLE 3. BFB KEY ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

4.12.5 **Data system:** A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library should also be available.

5.0 REAGENTS

5.1 Stock solutions: Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.1.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.1.2 Add the assayed reference material, as described below.

5.1.2.1 Liquids: Using a 100-uL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.1.2.2 Gases: To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0-mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.1.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (ug/uL) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.1.4 Transfer the stock standard solution into a Teflon-sealed screw cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.1.5 Prepare fresh standards every two months for gases. Reactive compounds such as 2-chloroethylvinyl ether and styrene may need to be prepared more frequently. All other standards must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.2 Secondary dilution standards: Using stock standard solutions, prepare in methanol secondary dilution standards containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.3 Surrogate standards: The surrogates recommended are toluene-d_8, 4-bromofluorobenzene, and 1,2-dichloroethane-d_4. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described in Section 5.1, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 250 ug/10 mL in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 uL of the surrogate spiking solution prior to analysis.

5.4 Internal standards: The recommended internal standards are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Sections 5.1 and 5.2. It is recommended that the secondary dilution standard should be prepared at a concentration of 25 ug/mL of each internal standard compound. Addition of 10 uL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 ug/L.

5.5 4-Bromofluorobenzene (BFB) standard: A standard solution containing 25 ng/uL of BFB in methanol should be prepared.

5.6 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared from the secondary dilution of stock standards (see Sections 5.1 and 5.2). Prepare these solutions in reagent water. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method (e.g., some or all of the compounds listed in Table 1 may be included). Store for one week only in a vial with no headspace.

5.7 Matrix spiking standards: Matrix spiking standards should be prepared from volatile organic compounds which will be representative of the compounds being investigated. The suggested compounds are 1,1-dichloroethene,

trichloroethene, chlorobenzene, toluene, and benzene. The standard should be prepared in methanol, with each compound present at a concentration of 250 ug/10.0 mL.

5.8 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standards be stored at -10°C to -20°C in screw-cap amber bottles with Teflon liners.

5.9 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit (MDL) of the parameters of interest.

5.9.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.9.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

5.9.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for 1 hr. While it is still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

5.10 Methanol: Pesticide quality or equivalent. Store apart from other solvents.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Direct injection: In very limited applications (e.g., aqueous process wastes), direct injection of the sample into the GC/MS system with a 10 uL syringe may be appropriate. One such application is for verification of the alcohol content of an aqueous sample prior to determining if the sample is ignitable (Methods 1010 or 1020). In this case, it is suggested that direct injection be used. The detection limit is very high (approximately 10,000 ug/L); therefore, it is only permitted when concentrations in excess of 10,000 ug/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.2 Initial calibration for purge-and-trap procedure:

7.2.1 **Recommended GC/MS operating conditions:**

Electron energy:	70 volts (nominal).
Mass range:	35-260 amu.
Scan time:	To give 5 scans/peak but not to exceed 7 sec/scan.
Initial column temperature:	45°C.
Initial column holding time:	3 min.
Column temperature program:	8°C/min.
Final column temperature:	220°C.
Final column holding time:	15 min.
Injector temperature:	200-225°C.
Source temperature:	According to manufacturer's specifications.
Transfer line temperature:	250-300°C.
Carrier gas:	Hydrogen at 50 cm/sec or helium at 30 cm/sec.

7.2.2 Each GC/MS system must be hardware-tuned to meet the criteria in Table 3 for a 50-ng injection or purging of 4-bromofluorobenzene (2-uL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.2.3 Assemble a purge-and-trap device that meets the specification in Section 4.11. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, condition the trap daily for 10 min while backflushing at 180°C with the column at 220°C.

7.2.4 Connect the purge-and-trap device to a gas chromatograph.

7.2.5 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device. Add 5.0 mL of reagent water to the purging device. The reagent water is added to the purging device using a 5-mL glass syringe fitted with a 15-cm 20-gauge needle. The needle is inserted through the sample inlet shown in Figure 1. The internal diameter of the 14-gauge needle that forms the sample inlet will permit insertion of the 20-gauge needle. Next, using a 10-uL or 25-uL micro-syringe equipped with a long needle (Paragraph 4.1), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards (Paragraph 5.6). Add the aliquot of calibration solution directly to the reagent water in the purging device by inserting the needle through the sample inlet. When discharging the contents of the micro-syringe, be sure that the end of the syringe needle is well beneath the surface of the reagent water. Similarly, add 10 uL of the internal standard solution (Paragraph 5.4). Close the 2-way syringe valve at the sample inlet.

7.2.6 Carry out the purge-and-trap analysis procedure as described in Section 7.4.1.

7.2.7 Tabulate the area response of the characteristic ions (see Table 1) against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured (Section 7.5.2). The RF is calculated as follows:

$$RF = (A_X C_{is})/(A_{is} C_X)$$

where:

A_X = Area of the characteristic ion for the compound being measured.

A_{is} = Area of the characteristic ion for the specific internal standard.

C_{is} = Concentration of the specific internal standard.

C_X = Concentration of the compound being measured.

7.2.8 The average RF must be calculated for each compound. A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. The minimum acceptable average RF for these compounds should be 0.300 (0.250 for bromoform). These compounds typically have RFs of 0.4-0.6 and are used to check compound instability and check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

7.2.8.1 Chloromethane: This compound is the most likely compound to be lost if the purge flow is too fast.

7.2.8.2 Bromoform: This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio may improve bromoform response.

7.2.8.3 Tetrachloroethane and 1,1-dichloroethane: These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.9 Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for Calibration Check Compounds (CCCs).

$$\%RSD = \frac{SD}{\bar{x}} \times 100$$

where:

RSD = relative standard deviation.

$\bar{x}$ = mean of 5 initial RFs for a compound.

SD = standard deviation of average RFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N - 1}}$$

The %RSD for each individual CCC should be less than 30 percent. This criterion must be met in order for the individual calibration to be valid. The CCCs are:

1,1-Dichloroethene,
Chloroform,
1,2-Dichloropropane,
Toluene,
Ethylbenzene, and
Vinyl chloride.

7.3 Daily GC/MS calibration:

7.3.1 Prior to the analysis of samples, inject or purge 50-ng of the 4-bromofluorobenzene standard. The resultant mass spectra for the BFB must meet all of the criteria given in Table 3 before sample analysis begins. These criteria must be demonstrated each 12-hr shift.

7.3.2 The initial calibration curve (Section 7.2) for each compound of interest must be checked and verified once every 12 hr of analysis time. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS by checking the SPCC (Paragraph 7.3.3) and CCC (Paragraph 7.3.4).

7.3.3 System Performance Check Compounds (SPCCs): A system performance check must be made each 12 hr. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum response factor for volatile SPCCs is 0.300 (0.250 for Bromoform). Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

7.3.4 **Calibration Check Compounds** (CCCs): After the system performance check is met, CCCs listed in Paragraph 7.2.9 are used to check the validity of the initial calibration. Calculate the percent difference using:

$$\% \text{ Difference} = \frac{\overline{RF}_I - RF_c}{\overline{RF}_I} \times 100$$

where:

$\overline{RF}_I$ = average response factor from initial calibration.

RF_c = response factor from current verification check standard.

If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than 25%, the initial calibration is assumed to be valid. If the criterion is not met (>25% difference), for any one CCC, corrective action MUST be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration MUST be generated. This criterion MUST be met before quantitative sample analysis begins.

7.3.5 The internal standard responses and retention times in the check calibration standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 sec from the last check calibration (12 hr), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning are necessary.

7.4 GC/MS analysis:

7.4.1 **Water samples:**

7.4.1.1 Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary and will prevent contamination of the purge-and-trap system. Two screening techniques that can be used are: the headspace sampler (Method 3810) using a gas chromatograph (GC) equipped with a photo ionization detector (PID) in series with an electrolytic conductivity detector (ECD); and extraction of the sample with hexadecane and analysis of the extract on a GC with a FID and/or an ECD (Method 3820).

7.4.1.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.4.1.3 Set up the GC/MS system as outlined in Paragraph 7.2.1.

7.4.1.4 BFB tuning criteria and daily GC/MS calibration criteria must be met (Section 7.3) before analyzing samples.

7.4.1.5 Adjust the purge gas (helium) flow rate to 25-40 mL/min on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response (see Section 7.2.8).

7.4.1.6 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hr. Care must be taken to prevent air from leaking into the syringe.

7.4.1.7 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

7.4.1.7.1 Dilutions may be made in volumetric flasks (10-to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.4.1.7.2 Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this quantity of reagent water to the flask.

7.4.1.7.3 Inject the proper aliquot of samples from the syringe prepared in Paragraph 7.4.1.6 into the flask. Aliquots of less than 1-mL are not recommended. Dilute the sample to the mark with reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.4.1.7.4 Fill a 5-mL syringe with the diluted sample as i n Paragraph 7.4.1.6.

7.4.1.8 Add 10.0 uL of surrogate spiking solution (Paragraph 5.3) and 10 uL of internal standard spiking solution (Paragraph 5.4) through the valve bore of the syringe; then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 uL of the surrogate spiking solution to 5 mL of sample is equivalent to a concentration of 50 ug/L of each surrogate standard.

7.4.1.9 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

7.4.1.10 Close both valves and purge the sample for 11.0 $\pm$ 0.1 min at ambient temperature.

7.4.1.11 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC/MS data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C while backflushing the trap with inert gas between 20 and 60 mL/min for 4 min. If this rapid heating requirement cannot be met, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the recommended initial program temperature of 45°C.

7.4.1.12 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5-mL flushes of reagent water (or methanol followed by reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

7.4.1.13 After desorbing the sample for 4 min, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 sec; then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C. Trap temperatures up to 220°C may be employed; however, the higher temperature will shorten the useful life of the trap. After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

7.4.1.14 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by a blank reagent water analysis. If the blank

analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

7.4.1.15 For matrix spike analysis, add 10 uL of the matrix spike solution (Paragraph 5.7) to the 5 mL of sample purged. Disregarding any dilutions, this is equivalent to a concentration of 50 ug/L of each matrix spike standard.

7.4.1.16 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Proceed to Sections 7.5.1 and 7.5.2 for qualitative and quantitative analysis.

7.4.2 **Water-miscible liquids:**

7.4.2.1 Water-miscible liquids are analyzed as water samples after first diluting them at least 50-fold with reagent water.

7.4.2.2 Initial and serial dilutions can be prepared by pipetting 2 mL of the sample to a 100-mL volumetric flask and diluting to volume with reagent water. Transfer immediately to a 5-mL gas-tight syringe.

7.4.2.3 Alternatively, prepare dilutions directly in a 5-mL syringe filled with reagent water by adding at least 20 uL, but not more than 100-uL of liquid sample. The sample is ready for addition of internal and surrogate standards.

7.4.3 **Sediment/soil and waste samples:** It is highly recommended that all samples of this type be screened prior to the purge-and-trap GC/MS analysis. The headspace method (Method 3810) or the hexadecane extraction and screening method (Method 3820) may used for this purpose. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and-trap system, and require extensive cleanup and instrument downtime. Use the screening data to determine whether to use the low-level method (0.005-1 mg/kg) or the high-level method (>1 mg/kg).

7.4.3.1 Low-level method: This is designed for samples containing individual purgeable compounds of <1 mg/kg. It is limited to sediment/soil samples and waste that is of a similar consistency (granular and porous). The low-level method is based on purging a heated sediment/soil sample mixed with reagent water containing the surrogate and internal standards. Analyze all reagent blanks and standards under the same conditions as the samples. See Figure 5 for an illustration of a low soils impinger.

7.4.3.1.1 Use a 5-g sample if the expected concentration is <0.1 mg/kg or a 1-g sample for expected concentrations between 0.1 and 1 mg/kg.

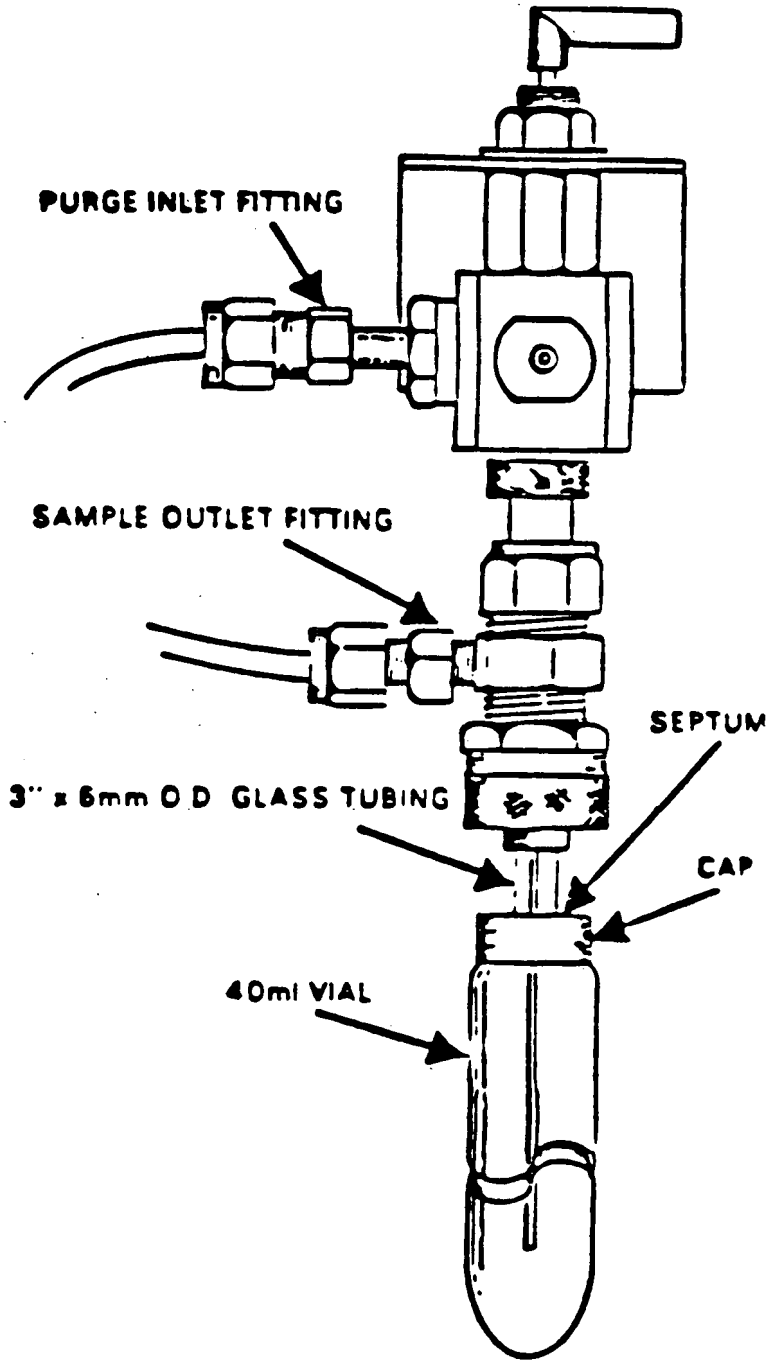


Figure 5. Low Soils Impinger

7.4.3.1.2 The GC/MS system should be set up as in Paragraphs 7.4.1.2-7.4.1.4. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and samples. A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed with the low-level method. Follow the initial and daily calibration instructions, except for the addition of a 40°C purge temperature.

7.4.3.1.3 Remove the plunger from a 5-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5.0 mL. Add 10 uL each of surrogate spiking solution (Paragraph 5.3) and internal standard solution (Paragraph 5.4) to the syringe through the valve. (Surrogate spiking solution and internal standard solution may be mixed together.) The addition of 10 uL of the surrogate spiking solution to 5 g of sediment/soil is equivalent to 50 ug/kg of each surrogate standard.

7.4.3.1.4 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount determined in Paragraph 7.4.3.1.1 into a tared purge device. Note and record the actual weight to the nearest 0.1 g.

7.4.3.1.5 Determine the percent moisture of the soil/sediment sample. This includes waste samples that are amenable to moisture determination. Other wastes should be reported on a wet-weight basis. Immediately after weighing the sample, weigh (to 0.1 g) 5-10 g of additional sediment/soil into a tared crucible. Dry the contents of the crucibles overnight at 105°C. Allow to cool in a desiccator and reweigh the dried contents. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\% \text{ moisture} = \frac{\text{grams of sample - grams of dry sample}}{\text{grams of sample}} \times 100$$

7.4.3.1.6 Add the spiked reagent water to the purge device, which contains the weighed amount of sample, and connect the device to the purge-and-trap system.

NOTE: Prior to the attachment of the purge device, the procedures in Paragraphs 7.4.3.1.4 and 7.4.3.1.6 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

7.4.3.1.7 Heat the sample to 40°C $\pm$ 1°C and purge the sample for 11.0 $\pm$ 0.1 min.

7.4.3.1.8 Proceed with the analysis as outlined in Paragraphs 7.4.1.11-7.4.1.16. Use 5 mL of the same reagent water as in the reagent blank. If saturated peaks occurred or would occur if a 1-g sample were analyzed, the medium-level method must be followed.

7.4.3.1.9 For low-level sediment/soils add 10 uL of the matrix spike solution (Paragraph 5.7) to the 5 mL of water (Paragraph 7.4.3.1.3). The concentration for a 5-g sample would be equivalent to 50 ug/kg of each matrix spike standard.

7.4.3.2 High-level method: The method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. An aliquot of the extract is added to reagent water containing surrogate and internal standards. This is purged at ambient temperature. All samples with an expected concentration of >1.0 mg/kg should be analyzed by this method.

7.4.3.2.1 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. For sediment/soil and waste that are insoluble in methanol weigh 4 g (wet weight) of sample into a tared 20-mL vial. Use a top-loading balance. Note and record the actual weight to 0.1 gram and determine the percent moisture of the sample using the procedure in Paragraph 7.4.3.1.5. For waste that is soluble in methanol, weigh 1 g (wet weight) into a tared scintillation vial or culture tube or a 10-mL volumetric flask. (If a vial or tube is used, it must be calibrated prior to use. Pipet 10.0 mL of methanol into the vial and mark the bottom of the meniscus. Discard this solvent.)

7.4.3.2.2 Quickly add 9.0 mL of methanol; then add 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 min.

NOTE: Steps 7.4.3.2.1 and 7.4.3.2.2 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.4.3.2.3 Pipet approximately 1 mL of the extract to a GC vial for storage, using a disposable pipet. The remainder may be disposed of. Transfer approximately 1 mL of reagent methanol to a separate GC vial for use as the method blank for each set of samples. These extracts may be stored at 4°C in the dark, prior to analysis. The addition of a 100-uL aliquot of each of these extracts in Paragraph 7.4.3.2.6 will give a concentration equivalent to 6,200 ug/kg of each surrogate standard.

7.4.3.2.4 The GC/MS system should be set up as in Paragraphs 7.4.1.2-7.4.1.4. This should be done prior to the addition of the methanol extract to reagent water.

7.4.3.2.5 Table 4 can be used to determine the volume of methanol extract to add to the 5 mL of reagent water for analysis. If a screening procedure was followed (Method 3810 or 3820), use the estimated concentration to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low-level analysis to determine the appropriate volume. If the sample was submitted as a medium-level sample, start with 100 uL. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.4.3.2.6 Remove the plunger from a 5.0-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of standards. Add 10 uL of internal standard solution. Also add the volume of methanol extract determined in Paragraph 7.4.3.2.5 and a volume of methanol solvent to total 100 uL (excluding methanol in standards).

7.4.3.2.7 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the water/methanol sample into the purging chamber.

7.4.3.2.8 Proceed with the analysis as outlined in Paragraphs 7.4.1.11-7.4.1.16. Analyze all reagent blanks on the same instrument as that use for the samples. The standards and blanks should also contain 100 uL of methanol to simulate the sample conditions.

7.4.3.2.9 For a matrix spike in the medium-level sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution (Paragraph 5.3), and 1.0 mL of matrix spike solution (Paragraph 5.7) as in Paragraph 7.4.3.2.2. This results in a 6,200 ug/kg concentration of each matrix spike standard when added to a 4-g sample. Add a 100-uL aliquot of this extract to 5 mL of water for purging (as per Paragraph 7.4.3.2.6).

TABLE 4. QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF MEDIUM-LEVEL SOILS/SEDIMENTS

Approximate Concentration Range	Volume of Methanol Extract[a]
500-10,000 ug/kg	100 uL
1,000-20,000 ug/kg	50 uL
5,000-100,000 ug/kg	10 uL
25,000-500,000 ug/kg	100 uL of 1/50 dilution [b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a]The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of methanol is necessary to maintain a volume of 100 uL added to the syringe.

[b]Dilute an aliquot of the methanol extract and then take 100 uL for analysis.

7.5 Data interpretation:

7.5.1 Qualitative analysis:

7.5.1.1 An analyte (e.g., those listed in Table 1) is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference should be obtained on the user's GC/MS within the same 12 hours as the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as those of the standard component; and (2) correspondence of the sample component and the standard component mass spectrum.

7.5.1.1.1 The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hr as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

7.5.1.1.2 (1) All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100% must be present in the sample spectrum). (2) The relative intensities of ions specified in (1) must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.

7.5.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

7.5.2 Quantitative analysis:

7.5.2.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantification will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (e.g., see Table 5).

7.5.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water and Water-Miscible Waste:

$$\text{concentration (ug/L)} = \frac{(A_x)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_x = Area of characteristic ion for compound being measured.

I_s = Amount of internal standard injected (ng).

A_{is} = Area of characteristic ion for the internal standard.

RF = Response factor for compound being measured (Paragraph 7.2.7).

V_o = Volume of water purged (mL), taking into consideration any dilutions made.

TABLE 5. VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

Bromochloromethane	1,4-Difluorobenzene
Acetone	Benzene
Acrolein	Bromodichloromethane
Acrylonitrile	Bromoform
Bromomethane	2-Butanone
Carbon disulfide	Carbon tetrachloride
Chloroethane	Chlorodibromomethane
Chloroform	2-Chloroethyl vinyl ether
Chloromethane	Dibromomethane
Dichlorodifluoromethane	1,4-Dichloro-2-butene
1,1-Dichloroethane	1,2-Dichloropropane
1,2-Dichloroethane	cis-1,3-Dichloropropene
1,2-Dichloroethane-d_4 (surrogate)	trans-1,3-Dichloropropene
1,1-Dichloroethene	1,1,1-Trichloroethane
trans-1,2-Dichloroethene	1,1,2-Trichloroethane
Iodomethane	Trichloroethene
Methylene chloride	Vinyl acetate
Trichlorofluoromethane	
Vinyl chloride	

Chlorobenzene-d_5
Bromofluorobenzene (surrogate)
Chlorobenzene
Ethylbenzene
Ethyl methacrylate
2-Hexanone
4-Methyl-2-pentanone
Styrene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
Toluene-d_8 (surrogate)
1,2,3-Trichloropropane
Xylene

Sediment/Soil, Sludge, and Waste:

High-level:

$$\text{concentration (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)}$$

Low-level:

$$\text{concentration (ug/kg)} = \frac{(A_x)(I_s)}{(A_{is})(RF)(W_s)}$$

where:

A_x, I_s, A_{is}, RF = same as for water.

V_t = volume of total extract (uL) (use 10,000 uL or a factor of this when dilutions are made).

V_i = volume of extract added (uL) for purging.

W_s = weight of sample extracted or purged (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.

7.5.2.3 Sediment/soil samples are generally reported on a dry weight basis, while sludges and wastes are reported on a wet weight basis. The % moisture of the sample (as calculated in Paragraph 7.4.3.1.5) should be reported along with the data in either instance.

7.5.2.4 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulas given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.5.2.5 Report results without correction for recovery data. When duplicates and spiked samples are analyzed, report all data obtained with the sample results.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing

analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.3 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still useable, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g, column changed), recalibration of the system must take place.

8.4 Required instrument QC is found in the following section:

8.4.1 The GC/MS system must be tuned to meet the BFB specifications in Section 7.2.2.

8.4.2 There must be an initial calibration of the GC/MS system as specified in 7.2.

8.4.3 The GC/MS system must meet the SPCC criteria specified in 7.3.3 and the CCC criteria in 7.3.4, each 12 hr.

8.5 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.5.1 A quality (QC) check sample concentrate is required containing each analyte at a concentration of 10 ug/mL in methanol. The QC check sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC check sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.5.2 Prepare a QC check sample to contain 20 ug/L of each analyte by adding 200 uL of QC check sample concentrate to 100 mL of reagent water.

8.5.3 Four 5-mL aliquots of the well-mixed QC check sample are analyzed according to the method beginning in Section 7.4.1.

8.5.4 Calculate the average recovery ($\bar{X}$) in ug/L, and the standard deviation of the recovery (s) in ug/L, for each analyte using the four results.

8.5.5 For each analyte compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and $\bar{X}$ for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined.

8.5.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Paragraph 8.5.6.1 or 8.5.6.2.

8.5.6.1 Locate and correct the source of the problem and repeat the test for all analytes beginning with Section 8.5.2.

8.5.6.2 Beginning with Section 8.5.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a reagent blank, a matrix spike, and a matrix spike duplicate/duplicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.6.1 The concentration of the spike in the sample should be determined as follows:

8.6.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in the sample is not being checked against a specific limit, the spike should be at 20 ug/L or 1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

TABLE 6. CALIBRATION AND QC ACCEPTANCE CRITERIA[a]

Parameter	Range for Q (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range p, p_s (%)
Benzene	12.8-27.2	6.9	15.2-26.0	37-151
Bromodichloromethane	13.1-26.9	6.4	10.1-28.0	35-155
Bromoform	14.2-25.8	5.4	11.4-31.1	45-169
Bromomethane	2.8-37.2	17.9	D-41.2	D-242
Carbon tetrachloride	14.6-25.4	5.2	17.2-23.5	70-140
Chlorobenzene	13.2-26.8	6.3	16.4-27.4	37-160
2-Chloroethylvinyl ether	D-44.8	25.9	D-50.4	D-305
Chloroform	13.5-26.5	6.1	13.7-24.2	51-138
Chloromethane	D-40.8	19.8	D-45.9	D-273
Dibromochloromethane	13.5-26.5	6.1	13.8-26.6	53-149
1,2-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7	18-190
1,3-Dichlorobenzene	14.6-25.4	5.5	17.0-28.8	59-156
1,4-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7	18-190
1,1-Dichloroethane	14.5-25.5	5.1	14.2-28.4	59-155
1,2-Dichloroethane	13.6-26.4	6.0	14.3-27.4	49-155
1,1-Dichloroethene	10.1-29.9	9.1	3.7-42.3	D-234
trans-1,2-Dichloroethene	13.9-26.1	5.7	13.6-28.4	54-156
1,2-Dichloropropane	6.8-33.2	13.8	3.8-36.2	D-210
cis-1,3-Dichloropropene	4.8-35.2	15.8	1.0-39.0	D-227
trans-1,3-Dichloropropene	10.0-30.0	10.4	7.6-32.4	17-183
Ethyl benzene	11.8-28.2	7.5	17.4-26.7	37-162
Methylene chloride	12.1-27.9	7.4	D-41.0	D-221
1,1,2,2-Tetrachloroethane	12.1-27.9	7.4	13.5-27.2	46-157
Tetrachloroethene	14.7-25.3	5.0	17.0-26.6	64-148
Toluene	14.9-25.1	4.8	16.6-26.7	47-150
1,1,1-Trichloroethane	15.0-25.0	4.6	13.7-30.1	52-162
1,1,2-Trichloroethane	14.2-25.8	5.5	14.3-27.1	52-150
Trichloroethene	13.3-26.7	6.6	18.5-27.6	71-157
Trichlorofluoromethane	9.6-30.4	10.0	8.9-31.5	17-181
Vinyl chloride	0.8-39.2	20.0	D-43.5	D-251

Q = Concentration measured in QC check sample, in ug/L.
s = Standard deviation of four recovery measurements, in ug/L.
$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.
p, p_s = Percent recovery measured.
D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 624 and were calculated assuming a QC check sample concentration of 20 ug/L. These criteria are based directly upon the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

8.6.2 Analyze one 5-mL sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC check sample concentrate (Section 8.5.1) appropriate for the background concentration in the sample. Spike a second 5-mL sample aliquot with 10 uL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A-B)%/T, where T is the known true value of the spike.

8.6.3 Compare the percent recovery (p) for each analyte with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be acounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 20 ug/L, the analyst must use either the QC acceptance criteria presented in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte: (1) Calculate accuracy (x') using the equation found in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting x' for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as (100x'/T) $\pm$ 2.44(100S'/T)%.

8.6.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed as described in Section 8.7.

8.7 If any analyte fails the acceptance criteria for recovery in Sectin 8.6, a QC check standard containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes in Table 6 must be measured in the sample in Section 8.6, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spiked sample.

8.7.1 Prepare the QC check standard by adding 10 uL of the QC check sample concentrate (Section 8.5.1 or 8.6.2) to 5 mL of reagent water. The QC check standard needs only to contain the analytes that failed criteria in the test in Section 8.6.

8.7.2 Analyze the QC check standard to determine the concentration measured (A) of each analyte. Calculate each precent recovery (p_s) as 100 (A/T)%, where T is the true value of the standard concentration.

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Benzene	0.93C+2.00	0.26$\bar{X}$-1.74	0.25$\bar{X}$-1.33
Bromodichloromethane	1.03C-1.58	0.15$\bar{X}$+0.59	0.20$\bar{X}$+1.13
Bromoform	1.18C-2.35	0.12$\bar{X}$+0.34	0.17$\bar{X}$+1.38
Bromomethane	1.00C	0.43$\bar{X}$	0.58$\bar{X}$
Carbon tetrachloride	1.10C-1.68	0.12$\bar{X}$+0.25	0.11$\bar{X}$+0.37
Chlorobenzene	0.98C+2.28	0.16$\bar{X}$-0.09	0.26$\bar{X}$-1.92
Chloroethane	1.18C+0.81	0.14$\bar{X}$+2.78	0.29$\bar{X}$+1.75
2-Chloroethylvinyl ether[a]	1.00C	0.62$\bar{X}$	0.84$\bar{X}$
Chloroform	0.93C+0.33	0.16$\bar{X}$+0.22	0.18$\bar{X}$+0.16
Chloromethane	1.03C-1.81	0.37$\bar{X}$+2.14	0.58$\bar{X}$+0.43
Dibromochloromethane	1.01C-0.03	0.17$\bar{X}$-0.18	0.17$\bar{X}$+0.49
1,2-Dichlorobenzene[b]	0.94C+4.47	0.22$\bar{X}$-1.45	0.30$\bar{X}$-1.20
1,3-Dichlorobenzene	1.06C+1.68	0.14$\bar{X}$-0.48	0.18$\bar{X}$-0.82
1,4-Dichlorobenzene[b]	0.94C+4.47	0.22$\bar{X}$-1.45	0.30$\bar{X}$-1.20
1,1-Dichloroethane	1.05C+0.36	0.13$\bar{X}$-0.05	0.16$\bar{X}$+0.47
1,2-Dichloroethane	1.02C+0.45	0.17$\bar{X}$-0.32	0.21$\bar{X}$-0.38
1,1-Dichloroethene	1.12C+0.61	0.17$\bar{X}$+1.06	0.43$\bar{X}$-0.22
trans-1,2,-Dichloroethene	1.05C+0.03	0.14$\bar{X}$+0.09	0.19$\bar{X}$+0.17
1,2-Dichloropropane[a]	1.00C	0.33$\bar{X}$	0.45$\bar{X}$
cis-1,3-Dichloropropene[a]	1.00C	0.38$\bar{X}$	0.52$\bar{X}$
trans-1,3-Dichloropropene[a]	1.00C	0.25$\bar{X}$	0.34$\bar{X}$
Ethyl benzene	0.98C+2.48	0.14$\bar{X}$+1.00	0.26$\bar{X}$-1.72
Methylene chloride	0.87C+1.88	0.15$\bar{X}$+1.07	0.32$\bar{X}$+4.00
1,1,2,2-Tetrachloroethane	0.93C+1.76	0.16$\bar{X}$+0.69	0.20$\bar{X}$+0.41
Tetrachloroethene	1.06C+0.60	0.13$\bar{X}$-0.18	0.16$\bar{X}$-0.45
Toluene	0.98C+2.03	0.15$\bar{X}$-0.71	0.22$\bar{X}$-1.71
1,1,1-Trichloroethane	1.06C+0.73	0.12$\bar{X}$-0.15	0.21$\bar{X}$-0.39
1,1,2-Trichloroethane	0.95C+1.71	0.14$\bar{X}$+0.02	0.18$\bar{X}$+0.00
Trichloroethene	1.04C+2.27	0.13$\bar{X}$+0.36	0.12$\bar{X}$+0.59
Trichlorofluoromethane	0.99C+0.39	0.33$\bar{X}$-1.48	0.34$\bar{X}$-0.39
Vinyl chloride	1.00C	0.48$\bar{X}$	0.65$\bar{X}$

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.
s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.
S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.
C = True value for the concentration, in ug/L.
$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.

[a]Estimates based upon the performance in a single laboratory.
[b]Due to chromatographic resolution problems, performance statements for these isomers are based upon the sums of their concentrations.

8.7.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in Table 6. Only analytes that failed the test in Section 8.6 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.8 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix) as in Section 8.6, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.9 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.9.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.9.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (p) and standard deviation of the percent recovery (s) for each of the surrogates.

8.9.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = $p + 3s$
Lower Control Limit (LCL) = $p - 3s$

8.9.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 8. The limits given in Table 8 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Paragraph 8.9.3 must fall within those given in Table 8 for these matrices.

8.9.5 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

TABLE 8. SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/Medium Water	Low/Medium Soil/Sediment
4-Bromofluorobenzene	86-115	74-121
1,2-Dichloroethane-d_4	76-114	70-121
Toluene-d_8	88-110	81-117

- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.9.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or a different ionization mode using a mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 This method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-600 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

10.0 REFERENCES

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2. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

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7. "Method Detection Limit for Methods 624 and 625," Olynyk, P., W.L. Budde, and J.W. Eichelberger, Unpublished report, October 1980.

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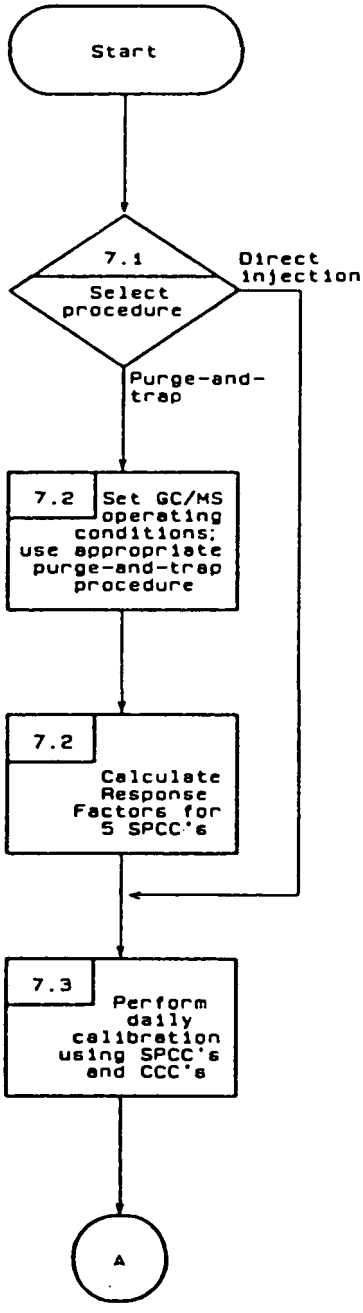
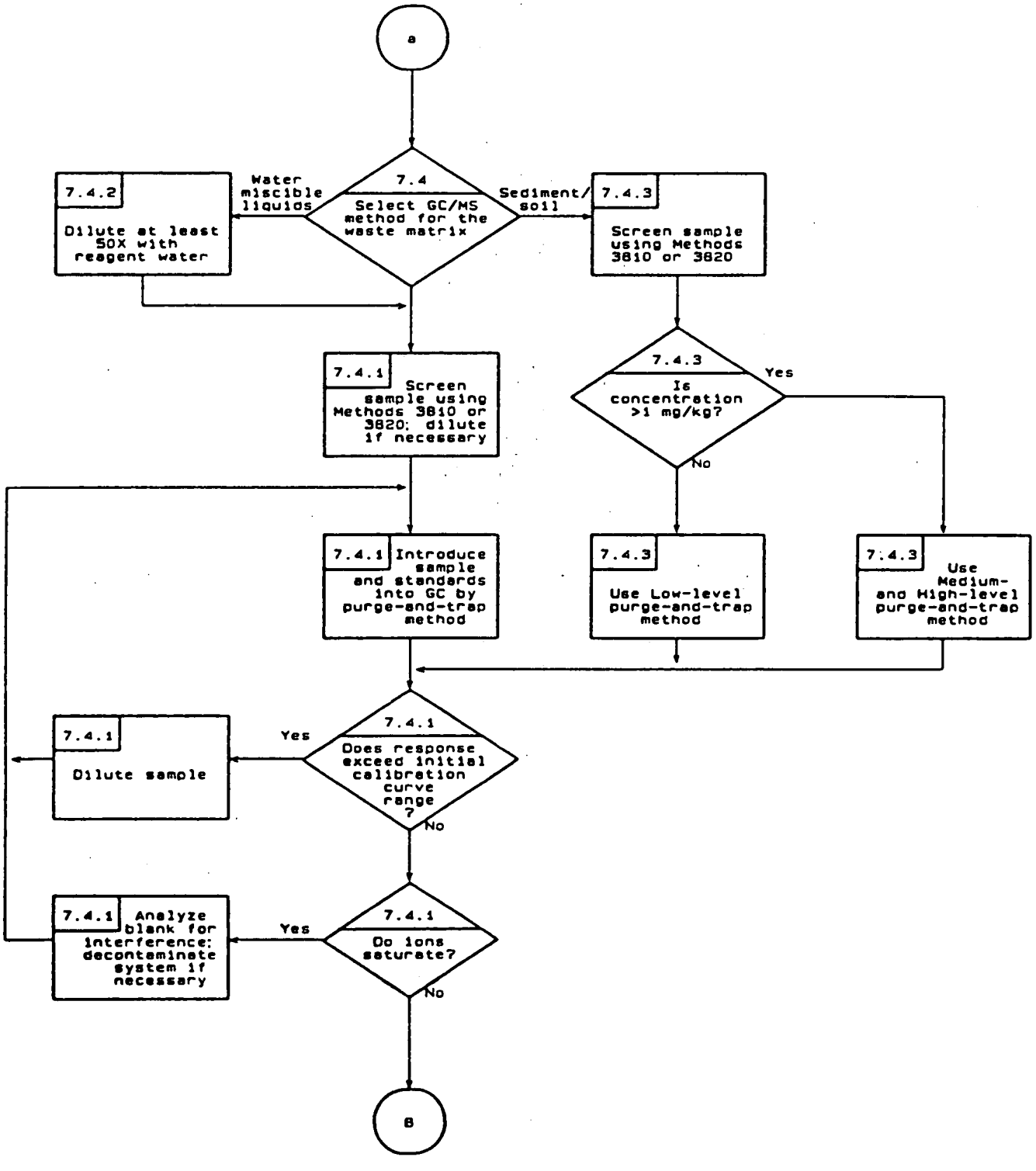
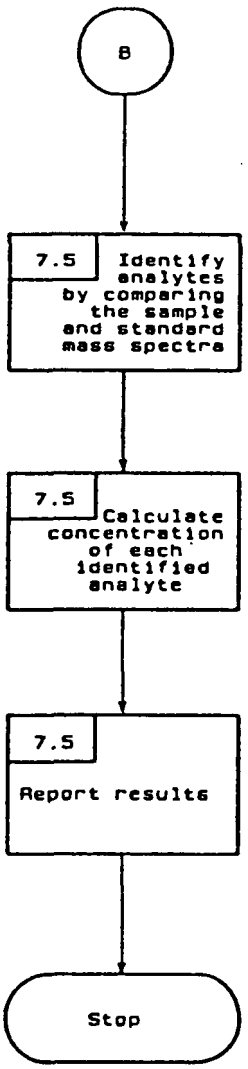
10. "Method Performance Data for Method 624," Memorandum from R. Slater and T. Pressley, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, January 17, 1984.


Start
7.1
Select procedure
Direct injection
Purge-and-trap
7.2
Set GC/MS operating conditions; use appropriate purge-and-trap procedure
7.2
Calculate Response Factors for 5 SPCC's
7.3
Perform daily calibration using SPCC's and CCC's
A


A
7.4
Select GC/MS method for the waste matrix
Water miscible liquids
Sediment/ soil
7.4.2
Dilute at least 50X with reagent water
7.4.3
Screen sample using Methods 3810 or 3820
7.4.1
Screen sample using Methods 3810 or 3820; dilute if necessary
7.4.3
Is concentration >1 mg/kg?
Yes
No
7.4.1
Introduce sample and standards into GC by purge-and-trap method
7.4.3
Use Low-level purge-and-trap method
7.4.3
Use Medium- and High-level purge-and-trap method
7.4.1
Does response exceed initial calibration curve range ?
Yes
No
7.4.1
Dilute sample
7.4.1
Do ions saturate?
Yes
No
7.4.1
Analyze blank for interference; decontaminate system if necessary
B


B
7.5
Identify analytes by comparing the sample and standard mass spectra
7.5
Calculate concentration of each identified analyte
7.5
Report results
Stop

METHOD 8250

GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR SEMIVOLATILE ORGANICS: PACKED COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8250 is used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and ground water. Direct injection of a sample may be used in limited applications.

1.2 Method 8250 can be used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic packed column. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system.

1.3 The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration. Also, chromatography is poor. Under the alkaline conditions of the extraction step, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected and are not being determined by Method 8080. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4 The practical quantitation limit (PQL) of Method 8250 for determining an individual compound is approximately 1 mg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 ug/L for ground water samples (see Table 2). PQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

TABLE 1. CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention Time (min)	Method detection limit (ug/L)	Primary Ion	Secondary Ion(s)
Acenaphthene	17.8	1.9	154	153, 152
Acenaphthene-d_{10} (I.S.)	--	--	164	162, 160
Acenaphthylene	17.4	3.5	152	151, 153
Acetophenone	--	--	105	77, 51
Aldrin	24.0	1.9	66	263, 220
Aniline	--	--	93	66, 65
Anthracene	22.8	1.9	178	176, 179
4-Aminobiphenyl	--	--	169	168, 170
Aroclor-1016[b]	18-30	--	222	260, 292
Aroclor-1221[b]	15-30	30	190	224, 260
Aroclor-1232[b]	15-32	--	190	224, 260
Aroclor-1242[b]	15-32	--	222	256, 292
Aroclor-1248[b]	12-34	--	292	362, 326
Aroclor-1254[b]	22-34	36	292	362, 326
Aroclor-1260[b]	23-32	--	360	362, 394
Benzidine[a]	28.8	44	184	92, 185
Benzoic acid	--	--	122	105, 77
Benzo(a)anthracene	31.5	7.8	228	229, 226
Benzo(b)fluoranthene	34.9	4.8	252	253, 125
Benzo(k)fluoranthene	34.9	2.5	252	253, 125
Benzo(g,h,i)perylene	45.1	4.1	276	138, 277
Benzo(a)pyrene	36.4	2.5	252	253, 125
Benzyl alcohol	--	--	108	79, 77
α-BHC[a]	21.1	--	183	181, 109
β-BHC	23.4	4.2	181	183, 109
δ-BHC	23.7	3.1	183	181, 109
γ-BHC (Lindane)[a]	22.4	--	183	181, 109
Bis(2-chloroethoxy)methane	12.2	5.3	93	95, 123
Bis(2-chloroethyl)ether	8.4	5.7	93	63, 95
Bis(2-chloroisopropyl)ether	9.3	5.7	45	77, 121
Bis(2-ethylhexyl)phthalate	30.6	2.5	149	167, 279
4-Bromophenyl phenyl ether	21.2	1.9	248	250, 141
Butyl benzyl phthalate	29.9	2.5	149	91, 206
Chlordane[b]	19-30	--	373	375, 377
4-Chloroaniline	--	--	127	129
1-Chloronaphthalene	--	--	162	127, 164
2-Chloronaphthalene	15.9	1.9	162	127, 164
4-Chloro-3-methylphenol	13.2	3.0	107	144, 142
2-Chlorophenol	5.9	3.3	128	64, 130
4-Chlorophenyl phenyl ether	19.5	4.2	204	206, 141
Chrysene	31.5	2.5	228	226, 229
Chrysene-d_{12} (I.S.)	--	--	240	120, 236
4,4'-DDD	28.6	2.8	235	237, 165
4,4'-DDE	27.2	5.6	246	248, 176

TABLE 1. - Continued

Compound	Retention Time (min)	Method detection limit (ug/L)	Primary Ion	Secondary Ion(s)
4,4'-DDT	29.3	4.7	235	237, 165
Dibenz(a,j)acridine	--	--	279	280, 277
Dibenz(a,h)anthracene	43.2	2.5	278	139, 279
Dibenzofuran	--	--	168	139
Di-n-butylphthalate	24.7	2.5	149	150, 104
1,3-Dichlorobenzene	7.4	1.9	146	148, 111
1,4-Dichlorobenzene	7.8	4.4	146	148, 111
1,4-Dichlorobenzene-d_4 (I.S.)	--	--	152	150, 115
1,2-Dichlorobenzene	8.4	1.9	146	148, 111
3,3'-Dichlorobenzidine	32.2	16.5	252	254, 126
2,4-Dichlorophenol	9.8	2.7	162	164, 98
2,6-Dichlorophenol	--	--	162	164, 98
Dieldrin	27.2	2.5	79	263, 279
Diethylphthalate	20.1	1.9	149	177, 150
p-Dimethylaminoazobenzene	--	--	120	225, 77
7,12-Dimethylbenz(a)anthracene	--	--	256	241, 257
α-,α-Dimethylphenethylamine	--	--	58	91, 42
2,4-Dimethylphenol	9.4	2.7	122	107, 121
Dimethylphthalate	18.3	1.6	163	194, 164
4,6-Dinitro-2-methylphenol	16.2	24	198	51, 105
2,4-Dinitrophenol	15.9	42	184	63, 154
2,4-Dinitrotoluene	19.8	5.7	165	63, 89
2,6-Dinitrotoluene	18.7	1.9	165	63, 89
Diphenylamine	--	--	169	168, 167
1,2-Diphenylhydrazine	--	--	77	105, 182
Di-n-octylphthalate	32.5	2.5	149	167, 43
Endosulfan I[a]	26.4	--	195	339, 341
Endosulfan II[a]	28.6	--	337	339, 341
Endosulfan sulfate	29.8	5.6	272	387, 422
Endrin[a]	27.9	--	263	82, 81
Endrin aldehyde	--	--	67	345, 250
Endrin ketone	--	--	317	67, 319
Ethyl methanesulfonate	--	--	79	109, 97
Fluoranthene	26.5	2.2	202	101, 203
Fluorene	19.5	1.9	166	165, 167
2-Fluorobiphenyl (surr.)	--	--	172	171
2-Fluorophenol (surr.)	--	--	112	64
Heptachlor	23.4	1.9	100	272, 274
Heptachlor epoxide	25.6	2.2	353	355, 351
Hexachlorobenzene	21.0	1.9	284	142, 249
Hexachlorobutadiene	11.4	0.9	225	223, 227
Hexachlorocyclopentadiene[a]	13.9	--	237	235, 272
Hexachloroethane	8.4	1.6	117	201, 199
Indeno(1,2,3-cd)pyrene	42.7	3.7	276	138, 227

TABLE 1. - Continued

Compound	Retention Time (min)	Method detection limit (ug/L)	Primary Ion	Secondary Ion(s)
Isophorone	11.9	2.2	82	95, 138
Methoxychlor	--	--	227	228
3-Methylcholanthrene	--	--	268	253, 267
Methyl methanesulfonate	--	--	80	79, 65
2-Methylnaphthalene	--	--	142	141
2-Methylphenol	--	--	108	107, 79
4-Methylphenol	--	--	108	107, 79
Naphthalene	12.1	1.6	128	129, 127
Naphthalene-d_8 (I.S.)	--	--	136	68
1-Naphthylamine	--	--	143	115, 116
2-Naphthylamine	--	--	143	115, 116
2-Nitroaniline	--	--	65	92, 138
3-Nitroaniline	--	--	138	108, 92
4-Nitroaniline	--	--	138	108, 92
Nitrobenzene	11.1	1.9	77	123, 65
Nitrobenzene-d_5 (surr.)	--	--	82	128, 54
2-Nitrophenol	6.5	3.6	139	109, 65
4-Nitrophenol	20.3	2.4	139	109, 65
N-Nitroso-di-n-butylamine	--	--	84	57, 41
N-Nitrosodimethylamine[a]	--	--	42	74, 44
N-Nitrosodiphenylamine[a]	20.5	1.9	169	168, 167
N-Nitroso-di-N-propylamine	--	--	70	130, 42
N-Nitrosopiperidine	--	--	42	114, 55
Pentachlorobenzene	--	--	250	252, 248
Pentachloronitrobenzene	--	--	295	237, 142
Pentachlorophenol	17.5	3.6	266	264, 268
Perylene-d_{12} (I.S.)	--	--	264	260, 265
Phenacetin	--	--	108	109, 179
Phenanthrene	22.8	5.4	178	179, 176
Phenanthrene-d_{10} (I.S.)	--	--	188	94, 80
Phenol	8.0	1.5	94	65, 66
Phenol-d_6 (surr.)	--	--	99	42, 71
2-Picoline	--	--	93	66, 92
Pronamide	--	--	173	175, 145
Pyrene	27.3	1.9	202	200, 203
Terphenyl-d_{14} (surr.)	--	--	244	122, 212
1,2,4,5-Tetrachlorobenzene	--	--	216	214, 218
2,3,4,6-Tetrachlorophenol	--	--	232	230, 131
2,4,6-Tribromophenol (surr.)	--	--	330	332, 141
1,2,4-Trichlorobenzene	11.6	1.9	180	182, 145
2,4,5-Trichlorophenol	--	--	196	198, 200
2,4,6-Trichlorophenol	11.8	2.7	196	198, 200
Toxaphene[b]	25-34	--	159	231, 233

[a]See Section 1.3
[b]These compounds are mixtures of various isomers.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

2.0 SUMMARY OF METHOD

2.1 Prior to using this method, the samples should be prepared for chromatography using the appropriate sample preparation and cleanup methods. This method describes chromatographic conditions that will allow for the separation of the compounds in the extract.

3.0 INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

3.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph/mass spectrometer system:

4.1.1 **Gas chromatograph:** An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases.

4.1.2 **Columns:**

4.1.2.1 For base/neutral compound detection: 2-m x 2-mm I.D. stainless or glass, packed with 3% SP-2250-DB on 100/120 mesh Supelcoport or equivalent.

4.1.2.2 For acid compound detection: 2-m x 2-mm I.D. glass, packed with 1% SP-1240-DA on 100/120 mesh Supelcoport or equivalent.

4.1.3 **Mass spectrometer:** Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 3 when 1 uL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

4.1.4 **GC/MS interface:** Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be

TABLE 3. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA [a]

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40-60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	>1% of mass 198
441	Present but less than mass 443
442	>40% of mass 198
443	17-23% of mass 442

[a] J.W. Eichelberger, L.E. Harris, and W.L. Budde. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry", Analytical Chemistry, 47, 995 (1975).

used. GC-to-MS interfaces constructed entirely of glass or glass-lined materials are recommended. Glass may be deactivated by silanizing with dichlorodimethylsilane.

4.1.5 **Data system:** A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library should also be available.

4.2 Syringe: 10-uL.

5.0 REAGENTS

5.1 Stock standard solutions (1.00 ug/uL): Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.1.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.1.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.1.3 Stock standard solutions must be replaced after 1 yr or sooner if comparison with quality control check samples indicates a problem.

5.2 Internal standard solutions: The internal standards recommended are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. Other compounds may be used as internal standards as long as the requirements given in Paragraph 7.3.2 are met. Dissolve 200 mg of each compound with a small volume of carbon disulfide. Transfer to a 50-mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is approximately 20% carbon disulfide.

Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. The resulting solution will contain each standard at a concentration of 4,000 ng/ul. Each 1-mL sample extract undergoing analysis should be spiked with 10 uL of the internal standard solution, resulting in a concentration of 40 ng/uL of each internal standard. Store at 4°C or less when not being used.

5.3 GC/MS tuning standard: A methylene chloride solution containing 50 ng/uL of decafluorotriphenylphosphine (DFTPP) should be prepared. The standard should also contain 50 ng/uL each of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Store at 4°C or less when not being used.

5.4 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared. One of the calibration standards should be at a concentration near, but above, the method detection limit; the others should correspond to the range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method (e.g., some or all of the compounds listed in Table 1 may be included). Each 1-mL aliquot of calibration standard should be spiked with 10 uL of the internal standard solution prior to analysis. All standards should be stored at -10°C to -20°C and should be freshly prepared once a year, or sooner if check standards indicate a problem. The daily calibration standard should be prepared weekly and stored at 4°C.

5.5 Surrogate standards: The recommended surrogate standards are phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. See Method 3500 for the instructions on preparing the surrogate standards. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all blanks, spikes, and sample extracts. Take into account all dilutions of sample extracts.

5.6 Matrix spike standards: See Method 3500 for instructions on preparing the matrix spike standard. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all blanks, spikes, and sample extracts. Take into account all dilutions of sample extracts.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sample preparation: Samples must be prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Water	3510, 3520
Soil/sediment	3540, 3550
Waste	3540, 3550, 3580

7.1.1 **Direct injection:** In very limited applications direct injection of the sample into the GC/MS system with a 10 uL syringe may be appropriate. The detection limit is very high (approximately 10,000 ug/L); therefore, it is only permitted where concentrations in excess of 10,000 ug/L are expected. The system must be calibrated by direct injection.

7.2 Extract cleanup: Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Compounds	Methods
Phenols	3630, 3640, 8040[a]
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3620, 3640, 3660
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorous pesticides	3620, 3640
Petroleum waste	3611, 3650
All priority pollutant base, neutral, and acids	3640

[a]Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered on GC/FID.

7.3 Initial calibration: The recommended GC/MS operating conditions:

Electron energy: 70 volts (nominal)
Mass range: 35-500 amu
Scan time: 1 sec/scan
Injector temperature: 250-300°C
Transfer line temperature: 250-300°C
Source temperature: According to manufacturer's specifications
Injector: Grob-type, splitless
Sample volume: 1-2 uL
Carrier gas: Helium at 30 mL/min

Conditions for base/neutral analysis (3% SP-2250-DB):

Initial column temperature and hold time: 50°C for 4 min
Column temperature program: 50-300°C at 8°C/min
Final column temperature hold: 300°C for 20 min

Conditions for acid analysis (1% SP-1240-DA):

Initial column temperature and hold time: 70°C for 2 min
Column temperature program: 70-200°C at 8°C/min
Final column temperature hold: 200°C for 20 min

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 3 for a 50-ng injection of DFTPP. Analyses should not begin until all these criteria are met. Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning.

7.3.2 The internal standards selected in Paragraph 5.1 should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion, i.e., for 1,4-dichlorobenzene-d_4 use m/z 152 for quantitation.

7.3.3 Analyze 1 uL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (as indicated in Table 1). Calculate response factors (RFs) for each compound as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$

where:

A_x = Area of the characteristic ion for the compound being measured.

A_{is} = Area of the characteristic ion for the specific internal standard.

C_x = Concentration of the compound being measured (ng/uL).

C_{is} = Concentration of the specific internal standard (ng/uL).

7.3.4 The average RF should be calculated for each compound. The percent relative standard deviation (%RSD = 100[SD/$\overline{RF}$]) should also be calculated for each compound. The %RSD should be less than 30% for each compound. However, the %RSD for each individual Calibration Check Compound (CCC) (see Table 4) must be less than 30%. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

7.3.5 A system performance check must be performed to ensure that minimum average response factors are met before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-nitroso-di-n-propylamine; hexachlorocyclopentadiene; 2,4-dinitrophenol; and 4-nitrophenol. The minimum acceptable average RF for these is 0.050. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

7.4 Daily GC/MS calibration:

7.4.1 Prior to analysis of samples, the GC/MS tuning standard must be analyzed. A 50-ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 3. These criteria must be demonstrated during each 12-hr shift.

7.4.2 A calibration standard(s) at mid-level concentration containing all semivolatile analytes, including all required surrogates, must be performed every 12-hr during analysis. Compare the response factor data from the standards every 12-hr with the average response factor from the initial calibration for a specific instrument as per SPCC (Paragraph 7.4.3) and CCC (Paragraph 7.4.4) criteria.

7.4.3 **System Performance Check Compounds** (SPCCs): A system performance check must be made during every 12 hr shift. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum RF for semivolatile SPCCs is 0.050. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins.

7.4.4 **Calibration Check Compounds** (CCCs): After the system performance check is met, CCCs listed in Table 4 are used to check the validity of the initial calibration. Calculate the percent difference using:

TABLE 4. CALIBRATION CHECK COMPOUNDS

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitroso-di-n-phenylamine	Phenol
Di-n-Octylphthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

$$\% \text{ Difference} = \frac{\overline{RF}_I - RF_C}{\overline{RF}_I} \times 100$$

where:

$\overline{RF}_I$ = average response factor from initial calibration.

RF_C = response factor from current verification check standard.

If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than 30%, the initial calibration is assumed to be valid. If the criterion is not met (>30% difference) for any one CCC, corrective action MUST be taken. Problems similar to those listed under SPCCs could affect these criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration MUST be generated. This criterion MUST be met before sample analysis begins.

7.4.5 The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 sec from the last check calibration (12 hr), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

7.5 GC/MS analysis:

7.5.1 It is highly recommended that the extract be screened on a GC/FID or GC/PID using the same type of column. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

7.5.2 Spike the 1-mL extract obtained from sample preparation with 10 uL of the internal standard solution just prior to analysis.

7.5.3 Analyze the 1-mL extract by GC/MS using the appropriate column (as specified in Paragraph 4.1.2). The recommended GC/MS operating conditions to be used are specified in Paragraph 7.3.

7.5.4 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 40 ng/uL of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

7.5.5 Perform all qualitative and quantitative measurements as described in Paragraph 7.6. Store the extracts at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

7.6 Data interpretation:

7.6.1 Qualitative analysis:

7.6.1.1 An analyte (e.g., those listed in Table 1) is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference compounds should be obtained on the user's GC/MS within the same 12 hours as the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as the standard component; and (2) correspondence of the sample component and the standard component mass spectrum.

7.6.1.1.1 The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hrs as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

7.6.1.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100% must be present in the sample spectrum.

7.6.1.1.3 The relative intensities of ions specified in Paragraph 7.6.1.1.2 must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.

7.6.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted (e.g., for EPA Contract Laboratory Program requirements, up to 20 substances of greatest apparent concentration not listed in the Hazardous Substance List must be tentatively identified). Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will

the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in sample the spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.6.2 **Quantitative analysis:**

7.6.2.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (e.g., see Table 5).

7.6.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water:

$$\text{concentration (ug/L)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_o)(V_i)}$$

where:

A_x = Area of characteristic ion for compound being measured.

I_s = Amount of internal standard injected (ng).

TABLE 5. SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl)ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl)ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethyl-phenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr.)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr.)
4-Methylphenol	Nitrobenzene	Hexachlorocyclo-pentadiene
N-Nitrosodimethylamine	Nitrobenzene-d_8 (surr.)	1-Naphthylamine
N-Nitroso-di-n-propylamine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitroso-di-n-butylamine	2-Nitroaniline
Phenol-d_6 (surr.)	N-Nitrosopiperidine	3-Nitroaniline
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetra-chlorobenzene
		2,3,4,6-Tetra-chlorophenol
		2,4,6-Tribromo-phenol (surr.)
		2,4,6-Trichloro-phenol
		2,4,5-Trichloro-phenol

(surr.) = surrogate

TABLE 5. SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION (Continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4-Aminobiphenyl	Benzidine	Benzo(b)fluoranthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl)phthalate	Benzo(g,h,i)perylene
Di-n-butyl phthalate	Butylbenzylphthalate	Benzo(a)pyrene
4,6-Dinitro-2-methylphenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)anthracene
1,2-Diphenylhydrazine	p-Dimethylaminoazobenzene	7,12-Dimethylbenz(a)anthracene
Fluoranthene	Pyrene	Di-n-octylphthalate
Hexachlorobenzene	Terphenyl-d_{14} (surr.)	Indeno(1,2,3-cd)pyrene
N-Nitrosodiphenylamine		3-Methylcholanthrene
Pentachlorophenol		
Pentachloronitrobenzene		
Phenacetin		
Phenanthrene		
Pronamide		

(surr.) = surrogate

V_t = Volume of total extract, taking into account dilutions (i.e., a 1-to-10 dilution of a 1-mL extract will mean V_t = 10,000 uL. If half the base/neutral extract and half the acid extract are combined, V_t = 2,000.

A_{is} = Area of characteristic ion for the internal standard.

RF = Response factor for compound being measured (Paragraph 7.3.3).

V_o = Volume of water extracted (mL).

V_i = Volume of extract injected (uL).

Sediment/Soil Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis):

$$\text{concentration (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)(D)}$$

where:

A_x, I_s, V_t, A_{is}, RF, V_i = same as for water.

W_s = weight of sample extracted or diluted in grams.

D = (100 - % moisture in sample)/100, or 1 for a wet-weight basis.

7.6.2.3 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulas given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.6.2.4 Report results without correction for recovery data. When duplicates and spiked samples are analyzed, report all data obtained with the sample results.

7.6.2.5 Quantitation of multicomponent compounds (e.g., Aroclors) is beyond the scope of Method 8270. Normally, quantitation is performed using a GC/ECD by Method 8080.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.3 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g, column changed), recalibration of the system must take place.

8.4 Required instrument QC is found in the following section:

8.4.1 The GC/MS system must be tuned to meet the DFTPP specifications in Section 7.3.1 and 7.4.1.

8.4.2 There must be an initial calibration of the GC/MS system as specified in 7.3.

8.4.3 The GC/MS system must meet the SPCC criteria specified in 7.4.3 and the CCC criteria in 7.4.4, each 12 hr.

8.5 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.5.1 A quality (QC) check sample concentrate is required containing each analyte at a concentration of 100 ug/mL in acetone. The QC check sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the

QC check sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.5.2 Using a pipet, prepare QC check samples at a concentration of 100 ug/L by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.5.3 Analyze the well-mixed QC check samples according to the method beginning in Section 7.1 with extraction of the samples.

8.5.4 Calculate the average recovery ($\bar{X}$) in ug/L, and the standard deviation of the recovery (s) in ug/L, for each analyte of interest using the four results.

8.5.5 For each analyte compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and $\bar{X}$ for all analytes of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are analyzed.

8.5.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.5.6.1 or 8.5.6.2.

8.5.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Section 8.5.2.

8.5.6.2 Beginning with Section 8.5.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a reagent blank, a matrix spike, and a matrix spike/duplicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.6.1 The concentration of the spike in the sample should be determined as follows:

8.6.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or

TABLE 6. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range p, p_s (%)
Acenaphthene	100	27.6	60.1-132.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Aldrin	100	39.0	7.2-152.2	D-166
Anthracene	100	32.0	43.4-118.0	27.133
Benzo(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-162
Benzo(a)pyrene	100	39.0	31.7-148.0	17-163
Benzo(ghi)perylene	100	58.9	D-195.0	D-219
Benzyl butyl phthalate	100	23.4	D-139.9	D-152
β-BHC	100	31.5	41.5-130.6	24-149
δ-BHC	100	21.6	D-100.0	D-110
Bis(2-chloroethyl)ether	100	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl)ether	100	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl)phthalate	100	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4	53-127
2-Chloronaphthalene	100	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158
Chrysene	100	48.3	44.1-139.9	17-168
4,4'-DDD	100	31.0	D-134.5	D-145
4,4'-DDE	100	32.0	19.2-119.7	4-136
4,4'-DDT	100	61.6	D-170.6	D-203
Dibenzo(a,h)anthracene	100	70.0	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3'-Dichlorobenzidine	100	71.4	8.2-212.5	D-262
Dieldrin	100	30.7	44.3-119.3	29-136
Diethyl phthalate	100	26.5	D-100.0	D-114
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
Di-n-octylphthalate	100	31.4	18.6-131.8	4-146
Endosulfan sulfate	100	16.7	D-103.5	D-107
Endrin aldehyde	100	32.5	D-188.8	D-209
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.6-108.4	59-121
Heptachlor	100	37.2	D-172.2	D-192
Heptachlor epoxide	100	54.7	70.9-109.4	26.155
Hexachlorobenzene	100	24.9	7.8-141.5	D-152
Hexachlorobutadiene	100	26.3	37.8-102.2	24-116
Hexachloroethane	100	24.5	55.2-100.0	40-113

TABLE 6. QC ACCEPTANCE CRITERIA[a] - Continued

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range p, p_s (%)
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Isophorone	100	63.3	46.6-180.2	21-196
Naphthalene	100	30.1	35.6-119.6	21-133
Nitrobenzene	100	39.3	54.3-157.6	35-180
N-Nitroso-di-n-propylamine	100	55.4	13.6-197.9	D-230
PCB-1260	100	54.2	19.3-121.0	D-164
Phenanthrene	100	20.6	65.2-108.7	54-120
Pyrene	100	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2	44-142
4-Chloro-3-methylphenol	100	37.2	40.8-127.9	22-147
2-Chlorophenol	100	28.7	36.2-120.4	23-134
2,4-Chlorophenol	100	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	100	26.1	41.8-109.0	32-119
2,4-Dinitrophenol	100	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0-100.0	D-181
2-Nitrophenol	100	35.2	45.0-166.7	29-182
4-Nitrophenol	100	47.2	13.0-106.5	D-132
Pentachlorophenol	100	48.9	38.1-151.8	14-176
Phenol	100	22.6	16.6-100.0	5-112
2,4,6-Trichlorophenol	100	31.7	52.4-129.2	37-144

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

p, p_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 625. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in the sample is not being checked against a limit specific to that analyte, the spike should be at 100 ug/L or 1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

8.6.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be at (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 ug/L.

8.6.2 Analyze one sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC check sample concentrate (Section 8.5.1) appropriate for the background concentration in the sample. Spike a second sample aliquot with 1.00 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A-B)%/T, where T is the known true value of the spike.

8.6.3 Compare the percent recovery (p) for each analyte with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 100 ug/L, the analyst must use either the QC acceptance criteria presented in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte: (1) Calculate accuracy (x') using the equation found in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting x' for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as $(100x'/T) \pm 2.44(100S'/T)\%$.

8.6.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed as described in Section 8.7.

8.7 If any analyte fails the acceptance criteria for recovery in Section 8.6, a QC check standard containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory.

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Acenaphthene	0.96C+0.19	0.15X-0.12	0.21X-0.67
Acenaphthylene	0.89C+0.74	0.24X-1.06	0.26X-0.54
Aldrin	0.78C+1.66	0.27X-1.28	0.43X+1.13
Anthracene	0.80C+0.68	0.21X-0.32	0.27X-0.64
Benzo(a)anthracene	0.88C-0.60	0.15X+0.93	0.26X-0.21
Chloroethane	0.99C-1.53	0.14X-0.13	0.17X-0.28
Benzo(b)fluoranthene	0.93C-1.80	0.22X+0.43	0.29X+0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19X+1.03	0.35X+0.40
Benzo(a)pyrene	0.90C-0.13	0.22X+0.48	0.32X+1.35
Benzo(ghi)perylene	0.98C-0.86	0.29X+2.40	0.51X-0.44
Benzyl butyl phthalate	0.66C-1.68	0.18X+0.94	0.53X+0.92
β-BHC	0.87C-0.94	0.20X-0.58	0.30X+1.94
δ-BHC	0.29C-1.09	0.34X+0.86	0.93X-0.17
Bis(2-chloroethyl)ether	0.86C-1.54	0.35X-0.99	0.35X+0.10
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16X+1.34	0.26X+2.01
Bis(2-chloroisopropyl)ether	1.03C-2.31	0.24X+0.28	0.25X+1.04
Bis(2-ethylhexyl)phthalate	0.84C-1.18	0.26X+0.73	0.36X+0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13X+0.66	0.16X+0.66
2-Chloronaphthalene	0.89C+0.01	0.07X+0.52	0.13X+0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20X-0.94	0.30X-0.46
Chrysene	0.93C-1.00	0.28X+0.13	0.33X-0.09
4,4'-DDD	0.56C-0.40	0.29X-0.32	0.66X-0.96
4,4'-DDE	0.70C-0.54	0.26X-1.17	0.39X-1.04
4,4'-DDT	0.79C-3.28	0.42X+0.19	0.65X-0.58
Dibenzo(a,h)anthracene	0.88C+4.72	0.30X+8.51	0.59X+0.25
Di-n-butyl phthalate	0.59C+0.71	0.13X+1.16	0.39X+0.60
1,2-Dichlorobenzene	0.80C+0.28	0.20X+0.47	0.24X+0.39
1,3-Dichlorobenzene	0.86C-0.70	0.25X+0.68	0.41X+0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24X+0.23	0.29X+0.36
3,3'-Dichlorobenzidine	1.23C-12.65	0.28X+7.33	0.47X+3.45
Dieldrin	0.82C-0.16	0.20X-0.16	0.26X-0.07
Diethyl phthalate	0.43C+1.00	0.28X+1.44	0.52X+0.22
Dimethyl phthalate	0.20C+1.03	0.54X+0.19	1.05X-0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12X+1.06	0.21X+1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14X+1.26	0.19X+0.35
Di-n-octylphthalate	0.76C-0.79	0.21X+1.19	0.37X+1.19
Endosulfan sulfate	0.39C+0.41	0.12X+2.47	0.63X-1.03
Endrin aldehyde	0.76C-3.86	0.18X+3.91	0.73X-0.62
Fluoranthene	0.81C+1.10	0.22X-0.73	0.28X-0.60
Fluorene	0.90C-0.00	0.12X+0.26	0.13X+0.61
Heptachlor	0.87C-2.97	0.24X-0.56	0.50X-0.23
Heptachlor epoxide	0.92C-1.87	0.33X-0.46	0.28X+0.64
Hexachlorobenzene	0.74C+0.66	0.18X-0.10	0.43X-0.52
Hexachlorobutadiene	0.71C-1.01	0.19X+0.92	0.26X+0.49
Hexachloroethane	0.73C-0.83	0.17X+0.67	0.17X+0.80

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a] - Continued

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Indeno(1,2,3-cd)pyrene	0.78C-3.10	0.29$\bar{X}$+1.46	0.50$\bar{X}$-0.44
Isophorone	1.12C+1.41	0.27$\bar{X}$+0.77	0.33$\bar{X}$+0.26
Naphthalene	0.76C+1.58	0.21$\bar{X}$-0.41	0.30$\bar{X}$-0.68
Nitrobenzene	1.09C-3.05	0.19$\bar{X}$+0.92	0.27$\bar{X}$+0.21
N-Nitroso-di-n-propylamine	1.12C-6.22	0.27$\bar{X}$+0.68	0.44$\bar{X}$+0.47
PCB-1260	0.81C-10.86	0.35$\bar{X}$+3.61	0.43$\bar{X}$+1.82
Phenanthrene	0.87C+0.06	0.12$\bar{X}$+0.57	0.15$\bar{X}$+0.25
Pyrene	0.84C-0.16	0.16$\bar{X}$+0.06	0.15$\bar{X}$+0.31
1,2,4-Trichlorobenzene	0.94C-0.79	0.15$\bar{X}$+0.85	0.21$\bar{X}$+0.39
4-Chloro-3-methylphenol	0.84C+0.35	0.23$\bar{X}$+0.75	0.29$\bar{X}$+1.31
2-Chlorophenol	0.78C+0.29	0.18$\bar{X}$+1.46	0.28$\bar{X}$+0.97
2,4-Dichlorophenol	0.87C-0.13	0.15$\bar{X}$+1.25	0.21$\bar{X}$+1.28
2,4-Dimethylphenol	0.71C+4.41	0.16$\bar{X}$+1.21	0.22$\bar{X}$+1.31
2,4-Dinitrophenol	0.81C-18.04	0.38$\bar{X}$+2.36	0.42$\bar{X}$+26.29
2-Methyl-4,6-dinitrophenol	1.04C-28.04	0.10$\bar{X}$+42.29	0.26$\bar{X}$+23.10
2-Nitrophenol	0.07C-1.15	0.16$\bar{X}$+1.94	0.27$\bar{X}$+2.60
4-Nitrophenol	0.61C-1.22	0.38$\bar{X}$+2.57	0.44$\bar{X}$+3.24
Pentachlorophenol	0.93C+1.99	0.24$\bar{X}$+3.03	0.30$\bar{X}$+4.33
Phenol	0.43C+1.26	0.26$\bar{X}$+0.73	0.35$\bar{X}$+0.58
2,4,6-Trichlorophenol	0.91C-0.18	0.16$\bar{X}$+2.22	0.22$\bar{X}$+1.81

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.

If the entire list of analytes in Table 6 must be measured in the sample in Section 8.6, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spiked sample.

8.7.1 Prepare the QC check standard by adding 1.0 mL of the QC check sample concentrate (Section 8.5.1 or 8.6.2) to 1 L of reagent water. The QC check standard needs only to contain the analytes that failed criteria in the test in Section 8.6.

8.7.2 Analyzed the QC check standard to determine the concentration measured (A) of each analyte. Calculate each percent recovery (P_s) as 100 (A/T)%, where T is the true value of the standard concentration.

8.7.3 Compare the percent recovery (P_s) for each analyte with the corresponding QC acceptance criteria found in Table 6. Only analytes that failed the test in Section 8.6 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.8 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix) as in Section 8.6, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p}$ = 90% and s_p = 10%, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.9 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.9.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.9.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (P) and standard deviation of the percent recovery (s) for each of the surrogates.

8.9.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = P + 3s
Lower Control Limit (LCL) = P - 3s

8.9.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 8. The limits given in Table 8 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Paragraph 8.9.3 must fall within those given in Table 8 for these matrices.

8.9.5 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.9.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or mass spectrometry using other ionization modes must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Method 8250 was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-1,300 ug/L. Single operator accuracy and precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act, Method 625," October 26, 1984.

TABLE 8. SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/Medium Water	Low/Medium Soil/Sediment
Nitrobenzene-d_5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
p-Terphenyl-d_{14}	33-141	18-137
Phenol-d_6	10-94	24-113
2-Fluorophenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122

2. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

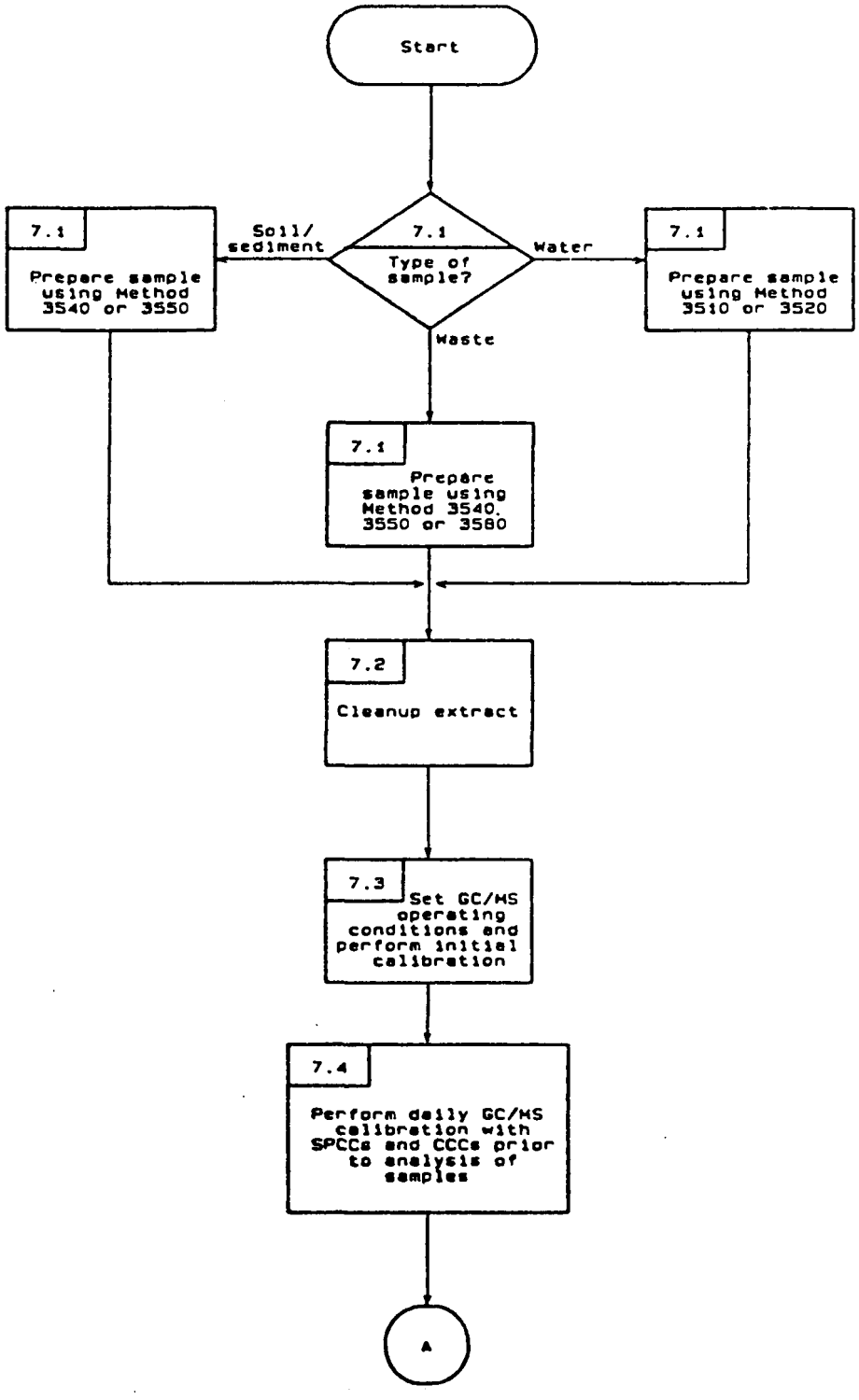
3. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, 58-63, 1983.

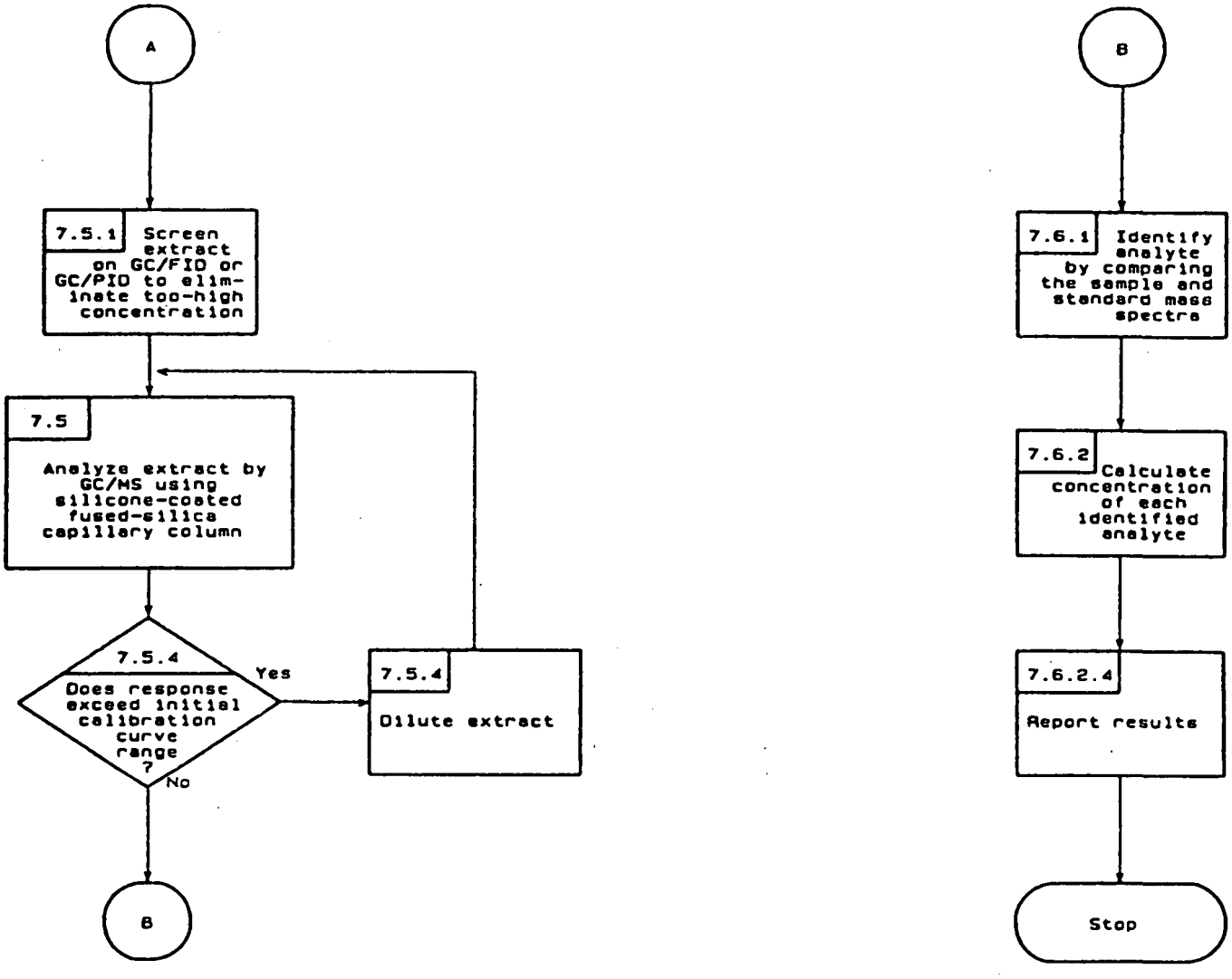
4. Eichelberger, J.W., L.E. Harris, and W.L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems," Analytical Chemistry, 47, 995-1000, 1975.

5. "Method Detection Limit for Methods 624 and 625," Olynyk, P., W.L. Budde, and J.W. Eichelberger, Unpublished report, October 1980.

6. "Interlaboratory Method Study for EPA Method 625-Base/Neutrals, Acids, and Pesticides," Final Report for EPA Contract 68-03-3102 (in preparation).

7. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.


Start
7.1
Type of sample?
Soil/ sediment
Water
Waste
7.1
Prepare sample using Method 3540 or 3550
7.1
Prepare sample using Method 3510 or 3520
7.1
Prepare sample using Method 3540, 3550 or 3580
7.2
Cleanup extract
7.3
Set GC/MS operating conditions and perform initial calibration
7.4
Perform daily GC/MS calibration with SPCCs and CCCs prior to analysis of samples
A


A
7.5.1 Screen extract on GC/FID or GC/PID to eliminate too-high concentration
7.5 Analyze extract by GC/MS using silicone-coated fused-silica capillary column
7.5.4 Does response exceed initial calibration curve range ?
Yes
No
7.5.4 Dilute extract
B
B
7.6.1 Identify analyte by comparing the sample and standard mass spectra
7.6.2 Calculate concentration of each identified analyte
7.6.2.4 Report results
Stop

METHOD 8260

GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR VOLATILE ORGANICS: CAPILLARY COLUMN TECHNIQUE

DRAFT

1.0 SCOPE AND APPLICATION

1.1 Method 8260 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

Analyte	CAS No.[a]
Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	156-69-4
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	594-20-7
1,1-Dichloropropene	563-58-6
Ethylbenzene	100-41-4
Hexachlorobutadiene	87-68-3

Analyte	CAS No.[a]
Isopropylbenzene	98-82-8
p-Isopropyltoluene	99-87-6
Methylene chloride	75-09-2
Naphthalene	91-20-3
n-Propylbenzene	103-65-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2,-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,2.3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropopane	96-18-4
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl chloride	75-01-4
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3

[a]Chemical Abstract Services Registry Number.

1.2 Method 8260 can be used to quantify most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, for the more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency. Such compounds include low-molecular-weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Tables 1 and 2 for lists of analytes and retention times that have been evaluated on a purge-and-trap GC/MS system. Also, the method detection limits for 25-mL sample volumes are presented.

1.3 The practical quantitation limit (PQL) of Method 8260 for an individual compound is approximately 5 ug/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 ug/L for ground water (see Table 3). PQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

1.4 Method 8260 is based upon a purge-and-trap, gas chromatographic/ mass spectrometric (GC/MS) procedure. This method is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by direct injection (in limited applications). Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb trapped sample components. The analytes are desorbed diretly to a large bore capillary or cryofocussed on a capillary precolumn before being flash evaporated to a narrow bore capillary for anaylsis. The column is temperature programmed to separate the analytes which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph. Wide bore capillary columns require a jet separator, whereas narrow bore capillary columns can be directly interfaced to the ion source.

2.2 If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in solvent to dissolve the volatile organic constituents. A portion of the solution is combined with water in the purge chamber. It is then analyzed by purge-and-trap GC/MS following the normal water method.

2.3 Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing resultant mass spectra and GC retention times. Each identified component is quantified by relating the MS response for an appropriate selected ion produced by that compound to the MS response for another ion produced by an internal standard.

3.0 INTERFERENCES

3.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter (Figure 1). Subtracting blank values from sample results is not permitted. If reporting values not corrected for blanks result in what the laboratory feels is a false positive for a sample, this should be fully explained in text accompanying the uncorrected data.

3.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. The preventive technique is rinsing of the purging apparatus and sample syringes with two portions of water between samples. After analysis of a sample containing high concentrations of volatile organic compounds, one or more calibration blanks should be analyzed to check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high levels of compounds being determined, it may be necessary to wash the purging device with a soap solution, rinse it with water, and then dry the purging device in an oven at 105°C. In extreme situations, the whole purge and trap device may require dismantling and

cleaning. Screening of the samples prior to purge and trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples. Screening may be accomplished with an automated headspace technique or by Method 3820 (Hexadecane Extraction and Screening of Purgeable Organics).

3.3 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean since clothing previously exposed to methylene chloride fumes during liquid/liquid extraction procedures can contribute to sample contamination.

3.4 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank prepared from water and carried through the sampling and handling protocol can serve as a check on such contamination.

4.0 APPARATUS AND MATERIALS

4.1 Purge-and-trap device - The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.1.1 The recommended purging chamber is designed to accept 5 mL (and 25 mL if the lowest detection limit is required) samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria. Alternate sample purge devices (i.e. needle spargers), may be utilized, provided equivalent performance is demonstrated.

4.1.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap must contain the following amounts of absorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap (see Figure 2). If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for

10 minutes at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples. Traps normally last 2-3 months when used daily. Some signs of a deteriorating trap are: uncharaceristic recoveries of surrogates, especially toluene-d_8; a loss of the response of the internal standards during a 12 hour shift; and/or a rise in the baseline in the early portion of the scan.

4.1.3 The desorber should be capable of rapidly heating the trap to 180°C for desorption. The trap bake-out temperature should not exceed 220°C. The desorber design illustrated in Figure 2 meets these criteria.

4.1.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 3 and 4.

4.1.5 Trap Packing Materials

4.1.5.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.1.5.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.1.5.3 Silica gel - 35/60 mesh, Davison, grade 15 or equivalent.

4.1.5.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 by crushing through a 26 mesh screen.

4.2 Heater or heated oil bath - Should be capable of maintaining the purging chamber to within 1°C over the temperature range of ambient to 100°C.

4.3 Gas chromatography/mass spectrometer/data system

4.3.1 The GC must be capable of temperature programming and should be equipped with variable constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation. For some column configuration, the column oven must be cooled to < 30°C, therefore, a subambient oven controller may be required. The GC is interfaced to the MS with an all glass enrichment device and an all glass transfer line, but any enrichment device or transfer line can be used if the performance specifications described in Step 8.2.4 can be achieved.

4.3.2 Gas chromatographic column 1 - 60 m x 0.75 mm i.d. VOCOL (Supelco) wide bore capillary column with 1.5 um film thickness. The flow rate of helium carrier gas is established at 15 mL/min. The column temperature is held for 5 minutes at 10°C, then programmed to 160°C at 6°C/min, and held until all expected compounds have eluted. A sample chromatogram obtained with this column is presented in Figure 5.

4.3.3 Gas chromatographic column 2 - 30 m x 0.53 mm i.d. DB-624 wide-bore (J&W Scientific) column with 3 um film thickness.

4.3.3.1 Cryogenic cooling - Helium carrier gas flow is 15 mL/min. The column temperature is held for 5 minutes at 10°C, then programmed to 160°C at 6°C/min. A sample chromatogram obtained with this column is presented in Figure 6.

4.3.3.2 Non-cryogenic cooling - It is recommended that carrier gas flow and split and make-up gases be set using performance of standards as guidance. Set the carrier gas head pressure to 10 psi and the split to 30 mL/min. Optimize the make-up gas flow for the separator (approximately 30 mL/min) by injecting BFB and determining the optimum response when varying the make-up gas. This will require several injections of BFB. Next, make several injections of the volatile working standard with all analytes of interst. Adjust the carrier and split to provide optimum chromatography and response. This is an especially critical adjustment for the volatile gas analytes. The head pressure should optimize between 8-12 psi and the split between 20-60 mL/min. The use of the splitter is important to minimize the effect of water on analyte response; to allow the use of a larger volume of helium during trap desorption; and to slow column flow. The column temperature is held for 2 minutes at 45°C, then programmed to 200°C at 8°C/min, and held for 6 minutes. A sample chromatogram is presented in Figure 7. A trap preheated to 150°C prior to trap desorption is required to provide adequate chromatography of the gas analytes.

4.3.4 Gas chromatographic column 3 - 30 m x 0.32 mm i.d. fused silica capillary column coated with Durabond DB-5 (J&W Scientific) with a 1 um film thickness. Helium carrier gas flow is 4 mL/min. The column is maintained at 10°C for 5 minutes, then programmed at 6°C/min for 10 minutes then 15°C/min for 5 minutes to 145°C. A sample chromatogram obtained with this column is presented in Figure 8.

4.3.5 Mass spectrometer - Mass spectral data are obtained with electron impact ionization at a nominal electron energy of 70 eV. The mass spectrometer must be capable of scanning from 35 to 300 amu every 2 seconds or less and must produce a mass spectrum that meets all criteria in Table 4 when 50 ng of 4-bromofluorobenzene is introduced into the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC. Injector temperature should be 200-225°C and transfer line temperature, 250-300°C. This includes, but is not limited to quadrupole, magnetic, ion trap, time of fight, and mixed analyzer (i.e. combined analyzers such as magnetic and quadrupole) mass spectrometers.

4.3.6 GC/MS interface - Any GC-to-MS interface that gives acceptable calibration points at 50 ng or less per injection for each of the analytes and achieves all acceptable performance criteria (see Table 4) may be used. GC-to-MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane. This interface is only needed for the wide bore columns ($\geq$ 0.53 mm i.d.).

4.3.7 Data system - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the NBS/EPA Mass Spectral Library should also be available.

4.4 Capillary precolumn interface when using cryogenic cooling - This device interfaces the purge and trap concentrator to the capillary gas chromatograph. The interface condenses the desorbed sample components and focuses them into a narrow band on an uncoated fused silica capillary precolumn. When the interface is flash heated, the sample is transferred to the analytical capillary column.

4.4.1 Under a stream of liquid nitgrogen, the temperature of the fused silica in the interface is maintained at -150°C during the cryofocussing step. After the desorption period, the interface must be capable of rapid heating to 250°C in 15 seconds or less to complete the transfer of analytes.

4.5 Microsyringes - 10, 25, 100, 250, 500, and 1,000-uL.

4.6 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.7 Syringes - 5, 10, or 25-mL, gas-tight with shutoff valve.

4.8 Balance - Analytical, capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.1 g.

4.9 Glass scintillation vials - 20-mL, with Teflon lined screw-caps or glass culture tubes with Teflon lined screw-caps.

4.10 Vials - 2-mL, for GC autosampler.

4.11 Disposable pipets - Pasteur.

5.0 REAGENTS

5.1 Methanol, CH_3OH. Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

5.2 Reagent Tetraglyme - Reagent tetraglyme is defined as tetraglyme in which interference is not observed at the method detection limit of compounds of interest.

CAUTION: Glycolethers are suspected carcinogens. All solvent handling should be done in a hood while using proper protective equipment to minimize exposure to liquid and vapor.

5.2.1 Tetraglyme (tetraethylene glycol dimethyl ether, Aldrich #17, 240-5 or equivalent), $C_8H_{18}O_5$. Purify by treatment at reduced pressure in a rotary evaporator. The tetraglyme should have a peroxide content of less than 5 ppm as indicated by EM Quant Test Strips (available from Scientific Products Co., Catalog No. P1126-8 or equivalent).

Peroxides may be removed by passing the tetraglyme through a column of activated alumina. The tetraglyme is placed in a round bottom flask equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90-100°C and a vacuum is maintained at < 10 mm Hg for at least two hours using a two-stage mechanical pump. The vacuum system is equipped with an all-glass trap, which is maintained in a dry ice/methanol bath. Cool the tetraglyme to ambient temperature and add 0.1 mg/mL of 2,6-di-tert-butyl-4-methyl-phenol to prevent peroxide formation. Store the tetraglyme in a tightly sealed screw-cap bottle in an area that is not contaminated by solvent vapors.

5.2.2 In order to demonstrate that all interfering volatiles have been removed from the tetraglyme, a water/tetraglyme blank must be analyzed.

5.3 Polyethylene glycol, reagent grade. Free of interferences at the detection limit of the analytes.

5.4 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.5 Hydrochloric acid (1:1), HCL. Carefully add a measured volume of concentrated HCL to an equal volume of water.

5.6 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified. Must be free of interferents at the method detection limit (MDL) of the analytes of interest. ASTM Type II water is further purified by any of the following techniques:

5.6.1 Water may be generated by passing tap water through a carbon filter bed containing about 450 g of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.6.2 A water purification system (Millipore Milli-Q Plus with the Organex-Q cartridge or equivalent) may be used to generate water.

5.6.3 Water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for 1 hour. While it is still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon lined septum and cap.

5.7 Stock solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.7.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.7.2 Add the assayed reference material, as described below.

5.7.2.1 Liquids - Using a 100-uL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.7.2.2 Gasses - To prepare standards for any compounds that boil below 30°C (e.g. bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0-mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.7.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (ug/uL) from the net gain in weight. When compound purity is assayed to be 90% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.7.4 Transfer the stock standard solution into a bottle with a Teflon lined screw-cap. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.7.5 Prepare fresh standards for gases every two months or sooner if comparison with check standards indicates a problem. Reactive compounds such as 2-chloroethylvinyl ether and styrene may need to be prepared more frequently. All other standards must be replaced after six months, or sooner if comparison with check standards indicates a problem. Both gas and liquid standards must be monitored closely by comparison to the initial calibration curve and by comparison to QC reference samples. It may be necessary to replace the standards more frequently if either check exceeds a 25% difference.

5.8 Secondary dilution standards - Using stock standard solutions, prepare in methanol, secondary dilution standards containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of

degradation or evaporation, especially just prior to preparing calibration standards from them. Store in a vial with no headspace for one week only.

5.9 Surrogate standards - The surrogates recommended are toluene-d_8, 4-bromofluorobenzene, and dibromofluoromethane. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described in Step 5.7, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 50-250 ug/10 mL in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 uL of the surrogate spiking solution prior to analysis.

5.10 Internal standards - The recommended internal standards are chlorobenzene-d_5, 1,4-difluorobenzene, 1,4-dichlorobenzene-d_4, and pentafluorobenzene. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Steps 5.7 and 5.8. It is recommended that the secondary dilution standard should be prepared at a concentration of 25 ug/mL of each internal standard compound. Addition of 10 uL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 ug/L.

5.11 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/uL of BFB in methanol should be prepared.

5.12 Calibration standards - Calibration standards at a minimum of five concentration levels should be prepared from the secondary dilution of stock standards (see Steps 5.7 and 5.8). Prepare these solutions in water. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method (e.g. some or all of the compounds listed in Table 1 may be included). Calibration standards must be prepared daily.

5.13 Matrix spiking standards - Matrix spiking standards should be prepared from volatile organic compounds which will be representative of the compounds being investigated. At a minimum, the matrix spike should include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. It is desirable to perform a matrix spike using compounds found in samples. Some permits may require spiking specific compounds of interest, especially if they are polar and would not be represented by the above listed compounds. The standard should be prepared in methanol, with each compound present at a concentration of 250 ug/10.0 mL.

5.14 Great care must be taken to maintain the integrity of all standard solutions. It is recommended all standards in methanol be stored at -10°C to -20°C in amber bottles with Teflon lined screw-caps.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Step 4.1.

7.0 PROCEDURE

7.1 Direct injection - In very limited appliations (e.g. aqueous process wastes) direct injection of the sample into the GC/MS system with a 10 uL syringe may be appropriate. One such application is for verification of the alcohol content of an aqueous sample prior to determining if the sample is ignitable (Methods 1010 or 1020). In this case, it is suggested that direct injection be used. The detection limit is very high (approximately 10,000 ug/L); therefore, it is only permitted when concentrations in excess of 10,000 ug/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection using the same solvent (e.g. water) for standards as the sample matrix (bypassing the purge-and-trap device).

7.2 Initial calibration for purge-and-trap procedure

7.2.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for a 50 ng injection or purging of 4-bromofluorobenzene (2 uL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.2.2 Assemble a purge-and-trap device that meets the specification in Step 4.1. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, condition the trap daily for 10 minutes while backflushing at 180°C with the column at 220°C.

7.2.3 Connect the purge-and-trap device to a gas chromatograph.

7.2.4 A set of at least five calibration standards containing the method analytes is needed. One calibration standard should contain each analyte at a concentration approaching but greater than the method detection limit (Table 1) for that compound; the other calibration standards should contain analytes at concentrations that define the range of the method. The purging efficiency for 5 mL of water is greater than for 25 mL, therefore, develop the standard curve with whichever volume of sample that will be analyzed. To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of water in a volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and should be prepared daily. Transfer 5.0 mL (or 25 mL if lower detection limits are required) of each standard to a gas tight syringe along with 10 uL of internal standard. Then transfer the contents to a purging device.

7.2.5 Carry out the purge-and-trap analysis procedure as described in Step 7.4.1.

7.2.6 Tabulate the area response of the characteristic ions (see Table 5) against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured (Step 7.5.2). The RF is calculated as follows:

$$RF = (A_X C_{is})/(A_{is} C_X)$$

where:

A_X = Area of the characteristic ion for the compound being measured.

A_{is} = Area of the characteristic ion for the specific internal standard.

C_{is} = Concentration of the specific internal standard.

C_X = Concentration of the compound being measured.

7.2.7 The average RF must be calculated for each compound and recorded on Form VI (see Chapter One). A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. The minimum acceptable average RF for these compounds should be 0.300 (0.250 for bromoform). These compounds typically have RFs of 0.4-0.6 and are used to check compound instability and check for degradation caused by contaminated lines or active sites in the system. Examples of these occurences are:

7.2.7.1 Chloromethane - This compound is the most likely compound to be lost if the purge flow is too fast.

7.2.7.2 Bromoform - This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve bromoform response.

7.2.7.3 Tetrachloroethane and 1,1-dichloroethane - These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.8 Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for Calibration Check Compounds (CCCs). Record the %RSDs for all compounds on Form VI (see Chapter One). The percent RSD is calculated as follows:

$$\%RSD = \frac{SD}{\bar{x}} \; 13 \times 100$$

where:

RSD = Relative standard deviation.

$\bar{x}$ = Mean of 5 initial RFs for a compound.

SD = Standard deviation of average RFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N - 1}}$$

The %RSD for each individual CCC must be less than 30 percent. This criterion must be met for the individual calibration to be valid. The CCCs are:

1,1-Dichloroethene,
Chloroform,
1,2-Dichloropropane,
Toluene,
Ethylbenzene, and
Vinyl chloride.

If the CCCs are not required analytes by the permit, then all required analytes must meet the 30% RSD criterion.

7.3 Daily GC/MS calibration

7.3.1 Prior to the analysis of samples, inject or purge 50-ng of the 4-bromofluorobenzene standard. The resultant mass spectra for the BFB must meet all of the criteria given in Table 4 before sample analysis begins. These criteria must be demonstrated each 12-hour shift.

7.3.2 The initial calibration curve (Step 7.2) for each compound of interest must be checked and verified once every 12 hours of analysis time. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS by checking the SPCC (Step 7.3.3) and CCC (Step 7.3.4).

7.3.3 System Performance Check Compounds (SPCCs) - A system performance check must be made each 12 hours. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum response factor for volatile SPCCs is 0.300 (0.250 for Bromoform). Some possible problems are standard mixture degration, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

7.3.4 Calibration Check Compounds (CCCs) - After the system performance check is met, CCCs listed in Step 7.2.8 are used to check the validity of the initial calibration. Calculate the percent difference using the following equation:

$$\% \text{ Difference} = \frac{\overline{RF}_I - RF_c}{\overline{RF}_I} \times 100$$

where:

$\overline{RF}_I$ = Average response factor from initial calibration.

RF_c = Response factor from current verification check standard.

If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than 25%, the initial calibration is assumed to be valid. If the criterion is not met (> 25% difference), for any one CCC, corrective action must be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration must be generated. This criterion must be met before quantitative sample analysis begins. If the CCCs are not required analytes by the permit, then all required analytes must meet the 25% difference criterion.

7.3.5 The internal standard responses and retention times in the check calibration standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last check calibration (12 hours), the chromatograhic system must be inspected for malfunctions and corections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning are necessary.

7.4 GC/MS analysis

7.4.1 Water samples

7.4.1.1 Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary and will prevent contamination of the purge-and-trap system. Two screening techniques that can be used are the headspace sampler (Method 3810) using a gas chromatograph (GC) equipped with a photo ionization detector (PID) in series with an electrolytic conductivity detector (ECD), and extraction of the sample with

hexadecane and analysis of the extract on a GC with a FID and/or an ECD (Method 3820).

7.4.1.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.4.1.3 Set up the GC/MS system as outlined in Step 4.3.

7.4.1.4 BFB tuning criteria and daily GC/MS calibration criteria must be met (Step 7.3) before analyzing samples.

7.4.1.5 Adjust the purge gas (helium) flow rate to 25-40 mL/min on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response (see Step 7.2.7).

7.4.1.6 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. If lower detection limits are required, use a 25-mL syringe. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

7.4.1.7 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

7.4.1.7.1 Dilutions may be made in volumetric flasks (10 to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.4.1.7.2 Calculate the approximate volume of water to be added to the volumetric flask selected and add slightly less than this quantity of water to the flask.

7.4.1.7.3 Inject the proper aliquot of samples from the syringe prepared in Step 7.4.1.6 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.4.1.7.4 Fill a 5-mL syringe with the diluted sample as in Step 7.4.1.6.

7.4.1.8. Compositing samples prior to GC/MS analysis

7.4.1.8.1 Add 5 mL or equal larger amounts of each sample (up to 5 samples are allowed) to a 25-mL glass syringe. Special precautions must be made to maintain zero headspace in the syringe.

7.4.1.8.2 The samples must be cooled at 4°C during this step to minimize volatilization losses.

7.4.1.8.3 Mix well and draw out a 5 mL aliquot for analysis.

7.4.1.8.4 Follow sample introduction, purging, and desorption steps described in the method.

7.4.1.8.5 If less than five samples are used for compositing, a proportionately smaller syringe may be used unless a 25 mL sample is to be purged.

7.4.1.9 Add 10.0 uL of surrogate spiking solution (Step 5.9) and 10 uL of internal standard spiking solution (Step 5.10) through the valve bore of the syringe; then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 uL of the surrogate spiking solution to 5 mL of sample is equivalent to a concentration of 50 ug/L of each surrogate standard.

7.4.1.10 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

7.4.1.11 Close both valves and purge the sample for 11.0 ± 0.1 minutes at ambient temperature. Be sure the trap is cooler than 25°C.

7.4.1.12 Sample desorption - The mode of sample desorption is determined by the type of capillary column employed for the analysis. When using a wide bore capillary column, follow the desorption conditions of Step 7.4.1.13. The conditions for using narrow bore columns are described in Step 7.4.1.14.

7.4.1.13 Sample desorption for wide bore capillary column. Under most conditions, this type of column must be interfaced to the MS through an all glass jet separator.

7.4.1.13.1 After the 11 minute purge, attach the trap to the chromatograph, adjust the purge and trap system to the desorb mode (Figure 4) and initiate the temperature program sequence of the gas chromatograph and start data acquisition. Introduce the trapped materials to the GC column by rapidly

heating the trap to 180°C while backflushing the trap with an inert gas at 15 mL/min for 4 minutes. If the non-cryogenic cooling technique is followed, the trap must be preheated to 150°C just prior to trap desorption at 180°C. While the purged analytes are being introduced into the gas chromatograph, empty the purging device using the sample syringe and wash the chamber with two 5 or 25 mL portions of water depending on the size of the purge device. After the purging device has been emptied, leave the syringe valve open to allow the purge gas to vent through the sample introduction needle.

7.4.1.13.2 Hold the column temperature at 10°C for 5 minutes, then program at 6°C/min to 160°C and hold until all analytes elute.

7.4.1.13.3 After desorbing the sample for 4 minutes, condition the trap by returning the purge-and-trap system to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately 7 minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

7.4.1.14 Sample desorption for narrow bore capillary column. Under normal operating conditions, most narrow bore capillary columns can be interfaced directly to the MS without a jet separator.

7.4.1.14.1 After the 11 minute purge, attach the trap to the cryogenically cooled interface at -150°C and adjust the purge-and-trap system to the desorb mode (Figure 4). Introduce the trapped materials to the interface by rapidly heating the trap to 180°C while backflushing the trap with an inert gas at 4 mL/min for 5 minutes. While the extracted sample is being introduced into the interface, empty the purging device using the sample syringe and rinse the chamber with two 5 or 25 mL portions of water depending on the size of the purging device. After the purging device has been emptied, leave the syringe valve open to allow the purge gas to vent through the sample introduction needle. After desorbing for 5 minutes, flash heat the interface to 250°C and quickly introduce the sample on the chromatographic column. Start the temperature program sequence, and initiate data acquisition.

7.4.1.14.2 Hold the column temperature at 10°C for 5 minutes, then program at 6°C/min to 70°C and then at 15°C/min to 145°C. After desorbing the sample for 5 minutes, recondition the trap by returning the purge-and-trap system to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately 15 minutes, turn off the trap heater and open the syringe valve to stop the gas

flow through the trap. When the trap is cool, the next sample can be analyzed.

7.4.1.15 If the initial analysis of the sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by a blank water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

7.4.1.16 For matrix spike analysis, add 10 uL of the matrix spike solution (Step 5.13) to the 5 mL of sample purged. Disregarding any dilutions, this is equivalent to a concentration of 50 ug/L of each matrix spike standard.

7.4.1.17 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Proceed to Steps 7.5.1 and 7.5.2 for qualitative and quantitative analysis.

7.4.2 Water-miscible liquids

7.4.2.1 Water-miscible liquids are analyzed as water samples after first diluting them at least 50-fold with water.

7.4.2.2 Initial and serial dilutions can be prepared by pipeting 2 mL of the sample to a 100-mL volumetric flask and diluting to volume with water. Transfer immediately to a 5-mL gas-tight syringe.

7.4.2.3 Alternatively, prepare dilutions directly in a 5-mL syringe filled with water by adding at least 20 uL, but not more than 100-uL of liquid sample. The sample is ready for addition of internal and surrogate standards.

7.4.3 Sediment/soil and waste samples - It is highly recommended that all samples of this type be screened prior to the purge-and-trap GC/MS analysis. The headspace method (Method 3810) or the hexadecane extraction and screening method (Method 3820) may used for this purpose. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and-trap system, and require extensive cleanup and instrument downtime. Use the screening data to determine whether to use the low-level method (0.005-1 mg/kg) or the high-level method (> 1 mg/kg).

7.4.3.1 Low-level method - This is designed for samples containing individual purgeable compounds of < 1 mg/kg. It is limited to sediment/soil samples and waste that is of a similar consistency (granular and porous). The low-level method is based on purging a

heated sediment/soil sample mixed with water containing the surrogate and internal standards. Analyze all blanks and standards under the same conditions as the samples. See Figure 9 for an illustration of a low soils impinger.

7.4.3.1.1 Use a 5 g sample if the expected concentration is < 0.1 mg/kg or a 1 g sample for expected concentrations between 0.1 and 1 mg/kg.

7.4.3.1.2 The GC/MS system should be set up as in Steps 7.4.1.3-7.4.1.4. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and samples. A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed with the low-level method. Follow the initial and daily calibration instructions, except for the addition of a 40°C purge temperature.

7.4.3.1.3 Remove the plunger from a 5-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5.0 mL. Add 10 uL each of surrogate spiking solution (Step 5.9) and internal standard solution (Step 5.10) to the syringe through the valve (surrogate spiking solution and internal standard solution may be mixed together). The addition of 10 uL of the surrogate spiking solution to 5 g of sediment/soil is equivalent to 50 ug/kg of each surrogate standard.

7.4.3.1.4 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount determined in Step 7.4.3.1.1 into a tared purge device. Note and record the actual weight to the nearest 0.1 g.

7.4.3.1.5 Determine the percent moisture of the soil/sediment sample. This includes waste samples that are amenable to moisture determination. Other wastes should be reported on a wet-weight basis. Immediately after weighing the sample, weigh (to 0.1 g) 5-10 g of additional sediment/soil into a tared crucible. Dry the contents of the crucibles overnight at 105°C. Allow to cool in a desiccator and reweigh the dried contents. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\% \text{ moisture} = \frac{\text{grams of sample} - \text{grams of dry sample}}{\text{grams of sample}} \times 100$$

7.4.3.1.6 Add the spiked water to the purging device, which contains the weighed amount of sample, and connect the device to the purge-and-trap system.

that has stringent control of

NOTE: Prior to the attachment of the purge device, the procedures in Steps 7.4.3.1.4 and 7.4.3.1.6 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory ~~free of~~ solvent vapors. There must be no solvents brought into the lab other than those used for extracting samples for volatiles or dissolving volatile standards (i.e. methanol, etc.). It is highly recommended that GC and GC/MS analysis for pesticides and semivolatiles be performed in a different room to avoid high background levels of methylene chloride and hexane.

7.4.3.1.7 Heat the sample to 40°C ± 1°C and purge the sample for 11.0 ± 0.1 minutes. Be sure the trap is cooler than 25°C.

7.4.3.1.8 Proceed with the analysis as outlined in Steps 7.4.1.12-7.4.1.17. Use 5 mL of the same water as in the blank. If saturated peaks occurred or would occur if a 1 g sample were analyzed, the medium-level method must be followed.

7.4.3.1.9 For low-level sediment/soils, add 10 uL of the matrix spike solution (Step 5.7) to the 5 mL of water (Step 7.4.3.1.3). The concentration for a 5 g sample would be equivalent to 50 ug/kg of each matrix spike standard.

7.4.3.2 High-level method - The method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. Wastes (i.e. petroleum and coke wastes) that are insoluble in methanol are diluted with tetraglyme or possibly polyethylene glycol (PEG). An aliquot of the extract is added to water containing surrogate and internal standards. This is purged at ambient temperature. All samples with an expected concentration of > 1.0 mg/kg should be analyzed by this method.

7.4.3.2.1 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. For sediment/soil and solid wastes that are insoluble in methanol weigh 4 g (wet weight) of sample into a tared 20-mL vial. Use a top-loading balance. Note and record the actual weight to 0.1 gram and determine the percent moisture of the sample using the procedure in Step 7.4.3.1.5. For waste that is soluble in methanol, tetraglyme, or PEG, weigh 1 g (wet weight) into a tared scintillation vial or culture tube or a 10-mL volumetric flask. (If a vial or tube is used, it must be calibrated prior to use. Pipet 10.0 mL of solvent into the vial and mark the bottom of the meniscus. Discard this solvent.)

7.4.3.2.2 Quickly add 9.0 mL of appropriate solvent. Cap and shake for 2 minutes.

that has stringent control of

NOTE: Steps 7.4.3.2.1 and 7.4.3.2.2 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory ~~free from~~ solvent vapors. There must be no solvents brought into the lab other than those used for extracting samples for volatiles or dissolving volatile standards (i.e. methanol, etc.). It is highly recommended that GC and GC/MS analysis for pesticides and semivolatiles be performed in a different room to avoid high background levels of methylene chloride and hexane.

7.4.3.2.3 Pipet approximately 1 mL of the extract to a GC vial for storage, using a disposable pipet. The remainder may be disposed. Transfer approximately 1 mL of appropriate solvent to a separate GC vial for use as the method blank for each set of samples. These extracts may be stored at 4°C in the dark, prior to analysis. The addition of a 100 uL aliquot of each of these extracts in Step 7.4.3.2.6 will give a concentration equivalent to 6,200 ug/kg of each surrogate standard.

7.4.3.2.4 The GC/MS system should be set up as in Steps 7.4.1.3-7.4.1.4. This should be done prior to the addition of the solvent extract to water.

7.4.3.2.5 The following information can be used to determine the volume of solvent extract to add to the 5 mL of water for analysis. If a screening procedure was followed (Method 3810 or 3820), use the estimated concentration to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low-level analysis to determine the appropriate volume. If the sample was submitted as a medium-level sample, start with 100 uL. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

QUANTITY OF EXTRACT REQUIRED FOR ANALYSIS OF HIGH-LEVEL SAMPLES

Approximate Concentration Range	Volume of Extract[a]
500- 10,000 ug/kg	100 uL
1,000- 20,000 ug/kg	50 uL
5,000-100,000 ug/kg	10 uL
25,000-500,000 ug/kg	100 uL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of solvent added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of solvent is necessary to maintain a volume of 100 uL added to the syringe.

[b] Dilute an aliquot of the solvent extract and then take 100 uL for analysis.

7.4.3.2.6 Remove the plunger from a 5.0-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of standards. Add 10 uL of internal standard solution; then add 10 uL of the surrogate spiking solution. Also add the volume of solvent extract determined in Step 7.4.3.2.5 and a volume of extraction or dissolution solvent to total 100 uL (excluding solvent in standards).

7.4.3.2.7 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the water/solvent sample into the purging chamber.

7.4.3.2.8 Proceed with the analysis as outlined in Steps 7.4.1.12-7.4.1.17. Analyze all blanks on the same instrument as that used for the samples. The standards and blanks should also contain 100 uL of the dilution solvent to simulate the sample conditions.

7.4.3.2.9 For a matrix spike in the medium-level sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution (Step 5.9), and 1.0 mL of matrix spike solution (Step 5.13) as in Step 7.4.3.2.2. This results in a 6,200 ug/kg concentration of each matrix spike standard when added to a 4 g sample. Add a 100 uL aliquot of this extract to 5 mL of water for purging (as per Step 7.4.3.2.6).

7.5 Data interpretation

7.5.1 Qualitative analysis

7.5.1.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum after background correction with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the analytical conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.5.1.1.1 The intensities of the characteristic ions of a compound maximize in the same or within one scan of each other. Selection of a peak by a data system target compound search

routine where the search is based on the presence of a chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.5.1.1.2 The RRT of the sample component is within 0.06 RRT units of the RRT of the standard component.

7.5.1.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.5.1.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.5.1.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e. a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e. only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.5.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within $\pm$ 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

7.5.2 Quantitative analysis

7.5.2.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantification will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (e.g. see Table 6).

7.5.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water and Water-Miscible Waste

$$\text{concentration (ug/L)} = \frac{(A_x)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_x = Area of characteristic ion for compound being measured.

I_s = Amount of internal standard injected (ng).

A_{is} = Area of characteristic ion for the internal standard.

RF = Response factor for compound being measured (Step 7.2.6).

V_o = Volume of water purged (mL), taking into consideration any dilutions made.

Sediment/Soil, Sludge, and Waste

High-level:

$$\text{concentration (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)}$$

Low-level:

$$\text{concentration (ug/kg)} = \frac{(A_x)(I_s)}{(A_{is})(RF)(W_s)}$$

where:

A_x, I_s, A_{is}, RF = Same as in water and water-miscble waste above.

V_t = Volume of total extract (uL) (use 10,000 uL or a factor of this when dilutions are made).

V_i = Volume of extract added (uL) for purging.

W_s = Weight of sample extracted or purged (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.

7.5.2.3 Sediment/soil samples are generally reported on a dry weight basis, while sludges and wastes are reported on a wet weight basis. The % moisture of the sample (as calculated in Step 7.4.3.1.5) should be reported along with the data in either instance.

7.5.2.4 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulas given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.5.2.5 Report results without correction for recovery data. When duplicates and spiked samples are analyzed, report all data obtained with the sample results.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the

performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a calibration blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent blank should be processed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.3 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still useable, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g. column changed), recalibration of the system must take place.

8.4 Required instrument QC

8.4.1 The GC/MS system must be tuned to meet the BFB specifications in Step 7.2.1.

8.4.2 There must be an initial calibration of the GC/MS system as specified in Step 7.2.

8.4.3 The GC/MS system must meet the SPCC criteria specified in Step 7.3.3 and the CCC criteria in Step 7.3.4, each 12 hours.

8.5 To establish the ability to generate acceptable accuracy and precision on water samples, the analyst must perform the following operations.

8.5.1 A quality control (QC) reference sample concentrate is required containing each analyte at a concentration of 10 ug/mL in methanol. The QC reference sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC reference sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.5.2 Prepare a QC reference sample to contain 20 ug/L of each analyte by adding 200 uL of QC reference sample concentrate to 100 mL of water. For the low level 25 mL a sample, spike at 5 ug/L.

8.5.3 Four 5 mL aliquots (or 25 mL for low level) of the well-mixed QC reference sample are analyzed according to the method beginning in Step 7.4.1.

8.5.4 Calculate the average percent recovery (R) and the standard deviation of the percent recovery (S_R), for the results. Ground water background corrections must be made before R and R_R calculation.

8.5.5 Tables 7 and 8 provide single laboratory recovery and precision data obtained for the method analytes from water. Similar results from dosed water should be expected by any experienced laboratory. Compare results obtained in Step 8.5.4 to the single laboratory recovery and precision data. If the results are not comparable, review potential problem areas and repeat the test. Results are comparable if the calculated percent relative standard deviation (RSD) does not exceed 2.6 times the single laboratory RSD or 20%, whichever is greater and the mean recovery lies within the interval R ± 3S or R ± 30%, which ever is greater.

8.5.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Step 8.5.6.1 or 8.5.6.2.

8.5.6.1 Locate and correct the source of the problem and repeat the test for all analytes beginning with Step 8.5.2.

8.5.6.2 Beginning with Step 8.5.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Step 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a blank and spiked replicates for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For soil and waste samples where detectable amounts of organics are present, replicate samples may be appropriate in place of spiked replicates. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.6.1 The concentration of the spike in the sample should be determined as follows:

8.6.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Step 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in a water sample is not being checked against a specific limit, the spike should be at 20 ug/L (or 5 ug/L for low level) or 1 to 5 times higher than the background concentration determined in Step 8.6.2, whichever concentration would be larger. For other matrices, the recommended spiking concentration is 10 times the PQL.

8.6.2 Analyze one 5 mL sample aliquot (or 25 mL for low level) to determine the background concentration (B) of each analyte. If necessary, prepare a new QC check sample concentrate (Step 8.5.1) appropriate for the background concentration in the sample. Spike a second 5 mL (or 25 mL for low level) sample aliquot with 10 uL of the QC reference sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A-B)%/T, where T is the known true value of the spike.

8.6.2.1 Compare the percent recovery (R_j) for each analyte with QC acceptance criteria established from the analyses of laboratory control standards (Step 8.5). Monitor all data from dosed samples. Analyte recoveries must fall within the established control limits.

8.6.2.2 If recovery is not within limits, the following procedures are required.

8.6.2.2.1 Check to be sure there are no errors in calculations, matrix spike solutions and internal standards. Also, check instrument performance.

8.6.2.2.2 Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

8.6.2.2.3 If the checks in 8.6.2.2.1 reveal no errors, the recovery problem encountered with the dosed sample is judged to be matrix-related, non system-related. The result for that analyte in the unspiked sample is labeled suspect/matrix to inform the user that the results are suspect due to matrix effects.

8.7 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix) as in Step 8.6, calculate the average percent recovery (p) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $p - 2s_p$ to $p + 2s_p$. If $p = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.8 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.8.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.8.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (p) and standard deviation of the percent recovery (s_p) for each of the surrogates.

8.8.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = $\bar{p} + 3s_p$
Lower Control Limit (LCL) = $\bar{p} - 3s_p$

8.8.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 9. The limits given in Table 9 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Step 8.8.3 must fall within those given in Table 9 for these matrices.

8.8.5 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.9.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or a different ionization mode using a mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

8.11 In recognition of the rapid advances occurring in chromatography, the analyst is permitted to modify GC columns, GC conditions, or detectors to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Step 8.4.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 This method has been tested in a single laboratory using spiked water. Using a wide-bore capillary column, water was spiked at concentrations between 0.5 and 10 ug/L. Single laboratory accuracy and precision data are presented for the method analytes in Table 7. Calculated MDLs are presented in Table 1.

9.3 The method was tested using water spiked at 0.1 to 0.5 ug/L and analyzed on a cryofocussed narrow-bore column. The accuracy and precision data for these compounds are presented in Table 8. MDL values were also calculated from these data and are presented in Table 2.

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TABLE 1.
CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON WIDE BORE CAPILLARY COLUMNS

ANALYTE	RETENTION TIME (minutes) Column 1[a]	Column 2[b]	Column 3[c]	MDL[d] (ug/L)
Dichlorodifluoromethane	1.55	0.70	--	0.10
Chloromethane	1.63	0.73	2.07	0.13
Vinyl Chloride	1.71	0.79	2.12	0.17
Bromomethane	2.01	0.96	2.26	0.11
Chloroethane	2.09	1.02	2.31	0.10
Trichlorofluoromethane	2.27	1.19	2.42	0.08
1,1-Dichloroethane	2.89	1.57	3.08	0.12
Methylene chloride	3.60	2.06	3.32	0.03
trans-1,2-Dichloroethene	3.98	2.36	3.48	0.06
1,1-Dichloroethane	4.85	2.93	4.10	0.04
2,2-Dichloropropane	6.01	3.80	4.43	0.35
cis-1,2-Dichloroethene	6.19	3.90	4.42	0.12
Chloroform	6.40	4.80	4.58	0.03
Bromochloromethane	6.74	4.38	4.54	0.04
1,1,1-Trichloroethane	7.27	4.84	5.09	0.08
Carbon tetrachloride	7.61	5.26	5.18	0.21
1,1-Dichloropropene	7.68	5.29	5.18	0.10
Benzene	8.23	5.67	5.29	0.04
1,2-Dichloroethane	8.40	5.83	5.29	0.06
Trichloroethene	9.59	7.27	6.07	0.19
1,2-Dichloropropane	10.09	7.66	6.20	0.04
Bromodichloromethane	10.59	8.49	6.39	0.08
Dibromomethane	10.65	7.93	6.27	0.24
Toluene	12.43	10.00	7.36	0.11
1,1,2-Trichloroethane	13.41	11.05	8.07	0.10
Tetrachloroethene	13.74	11.15	8.21	0.14
1,3-Dichloropropane	14.04	11.31	8.20	0.04
Dibromochloromethane	14.39	11.85	8.39	0.05
1,2-Dibromoethane	14.73	11.83	--	0.06
1-Chlorohexane	15.46	13.29	--	0.05
Chlorobenzene	15.76	13.01	9.33	0.04
1,1,1,2-Tetrachloroethane	15.94	13.33	9.41	0.05
Ethylbenzene	15.99	13.39	9.44	0.06
p-Xylene	16.12	13.69	9.56	0.13
m-Xylene	16.17	13.68	9.56	0.05
o-Xylene	17.11	14.52	10.32	0.11
Styrene	17.31	14.60	10.33	0.04
Bromoform	17.93	14.88	10.48	0.12
Isopropylbenzene	18.06	15.46	--	0.15
1,1,2,2-Tetrachloroethane	18.72	16.35	11.38	0.04
Bromobenzene	18.95	15.86	11.35	0.03

TABLE 1.
(Continued)

ANALYTE	RETENTION TIME (minutes) Column 1[a]	Column 2[b]	Column 3[c]	MDL[d] (ug/L)
1,2,3-Trichloropropane	19.02	16.23	11.40	0.32
n-Propylbenzene	19.06	16.41	--	0.04
2-Chlorotoluene	19.34	16.42	11.57	0.04
1,3,5-Trimethylbenzene	19.47	16.90	--	0.05
4-Chlorotoluene	19.50	16.72	12.08	0.06
tert-Butylbenzene	20.28	17.57	--	0.14
1,2,4-Trimethylbenzene	20.34	17.70	--	0.13
sec-Butylbenzene	20.79	18.09	--	0.13
p-Isopropyltoluene	21.20	18.52	--	0.12
1,3-Dichlorobenzene	21.22	18.14	13.16	0.12
1,4-Dichlorobenzene	21.55	18.39	13.27	0.03
n-Butylbenzene	22.22	19.49	--	0.11
1,2-Dichlorobenzene	22.52	19.17	14.10	0.03
1,2-Dibromo-3-chloropropane	24.53	21.08	--	0.26
1,2,4-Trichlorobenzene	26.55	23.08	--	0.04
Hexachlorobutadiene	26.99	23.68	--	0.11
Naphthalene	27.17	23.52	--	0.04
1,2,3-Trichlorobenzene	27.78	24.18	--	0.03
INTERNAL STANDARDS/SURROGATES				
4-Bromofluorobenzene	18.63	15.71	11.22	

[a]Column 1 - 60 m x 0.75 mm i.d. VOCOL capillary. Hold at 10°C for 5 minutes, then program to 160°C at 6°/min.

[b]Column 2 - 30 m x 0.53 mm i.d. DB-624 wide-bore capillary using cryogenic oven. Hold at 10°C for 5 minutes, then program to 160°C at 6°/min.

[c]Column 3 - 30 m x 0.53 mm i.d. DB-624 wide-bore capillary, cooling GC oven to ambient temperatures. Hold at 45°C for 2 minutes, then program to 200°C at 8°/min and hold for 6 minutes.

[d]MDL based on a 25 mL sample volume.

TABLE 2.
CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON NARROW-BORE CAPILLARY COLUMNS

ANALYTE	RETENTION TIME (minutes) Column 3[a]	MDL[b] (ug/L)
Dichlorodifluoromethane	0.88	0.11
Chloromethane	0.97	0.05
Vinyl chloride	1.04	0.04
Bromomethane	1.29	0.06
Chloroethane	1.45	0.02
Trichlorofluoromethane	1.77	0.07
1,1-Dichloroethene	2.33	0.05
Methylene chloride	2.66	0.09
trans-1,2-Dichloroethene	3.54	0.03
1,1-Dichloroethane	4.03	0.03
cis-1,2-Dichloroethene	5.07	0.06
2,2-Dichloropropane	5.31	0.08
Chloroform	5.55	0.04
Bromochloromethane	5.63	0.09
1,1,1-Trichloroethane	6.76	0.04
1,2-Dichloroethane	7.00	0.02
1,1-Dichloropropene	7.16	0.12
Carbon tetrachloride	7.41	0.02
Benzene	7.41	0.03
1,2-Dichloropropane	8.94	0.02
Trichloroethene	9.02	0.02
Dibromomethane	9.09	0.01
Bromodichloromethane	9.34	0.03
Toluene	11.51	0.08
1,1,2-Trichloroethane	11.99	0.08
1,3-Dichloropropane	12.48	0.08
Dibromochloromethane	12.80	0.07
Tetrachloroethene	13.20	0.05
1,2-Dibromoethane	13.60	0.10
Chlorobenzene	14.33	0.03
1,1,1,2-Tetrachloroethane	14.73	0.07
Ethylbenzene	14.73	0.03
p-Xylene	15.30	0.06
m-Xylene	15.30	0.03
Bromoform	15.70	0.20
o-Xylene	15.78	0.06
Styrene	15.78	0.27
1,1,2,2-Tetrachloroethane	15.78	0.20
1,2,3-Trichloropropane	16.26	0.09
Isopropylbenzene	16.42	0.10

TABLE 2.
(Continued)

ANALYTE	RETENTION TIME (minutes) Column 3[a]	MDL[b] (ug/L)
Bromobenzene	16.42	0.11
2-Chlorotoluene	16.74	0.08
n-Propylbenzene	16.82	0.10
4-Chlorotoluene	16.82	0.06
1,3,5-Trimethylbenzene	16.99	0.06
tert-Butylbenzene	17.31	0.33
1,2,4-Trimethylbenzene	17.31	0.09
sec-Butylbenzene	17.47	0.12
1,3-Dichlorobenzene	17.47	0.05
p-Isopropyltoluene	17.63	0.26
1,4-Dichlorobenzene	17.63	0.04
1,2-Dichlorobenzene	17.79	0.05
n-Butylbenzene	17.95	0.10
1,2-Dibromo-3-chloropropane	18.03	0.50
1,2,4-Trichlorobenzene	18.84	0.20
Naphthalene	19.07	0.10
Hexachlorobutadiene	19.24	0.10
1,2,3-Trichlorobenzene	19.24	0.14

[a]Column 3 - 30 m x 0.32 mm i.d. DB-5 capillary with um film thickness.

[b]MDL based on a 25 mL sample volume.

TABLE 3.
PRACTICAL QUANTITATION LIMITS FOR VOLATILE ANALYTES[a]

	Practical Quantitation Limits		
	Ground water		Low Soil/Sediment[b]
	ug/L		ug/kg
Volume of water purged	5 mL	25 mL	
All analytes in Table 1	5	1	5

[a]Practical Quantitation Limit (PQL) - The lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The PQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the PQL analyte level is selected for the lowest non-zero standard in the calibration curve. Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achieveable. See the following information for further guidance on matrix-dependent PQLs.

[b]PQLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis; therefore, PQLs will be higher, based on the % moisture in each sample.

Other Matrices:	Factor[c]
Water miscible liquid waste	50
High-level soil and sludges	125
Non-water miscible waste	500

[c]PQL = [PQL for low soil sediment (Table 3)] X [Factor]. For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 4.
BFB MASS - INTENSITY SPECIFICATIONS (4-BROMOFLUOROBENZENE)

Mass	Intensity Required (relative abundance)
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

TABLE 5.
CHARACTERISTIC MASSES (M/Z) FOR PURGEABLE ORGANIC COMPOUNDS

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Benzene	78	-
Bromobenzene	156	77,158
Bromochloromethane	128	49,130
Bromodichloromethane	83	85,127
Bromoform	173	175,254
Bromomethane	94	96
n-Butylbenzene	91	92,134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91,134
Carbon tetrachloride	117	119
Chlorobenzene	112	77,114
Chloroethane	64	66
Chloroform	83	85
Chloromethane	50	52
2-Chlorotoluene	126	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155,157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109,188
Dibromomethane	93	95,174
1,2-Dichlorobenzene	146	111,148
1,3-Dichlorobenzene	146	111,148
1,4-Dichlorobenzene	146	111,148
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65,83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61,63
cis-1,2-Dichloroethene	96	61,98
trans-1,2-Dichloroethene	96	61,98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,1-Dichloropropene	75	110,77
Ethylbenzene	91	106
Hexachlorobutadiene	225	223,227
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134,91
Methylene chloride	84	86,49
Naphthalene	128	-
n-Propylbenzene	120	120
Styrene	104	78
1,1,1,2-Tetrachloroethane	131	133,119

TABLE 5.
(Continued)

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion(s)
1,1,1,2-Tetrachloroethane	83	131,85
Tetrachloroethene	166	168,129
Toluene	92	91
1,2,3-Trichlorobenzene	180	182,145
1,2,4-Trichlorobenzene	180	182,145
1,1,1-Trichloroethane	97	99,61
1,1,2-Trichloroethane	83	97,85
Trichloroethene	95	130,132
Trichlorofluoromethane	101	103
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
INTERNAL STANDARDS/SURROGATES		
4-Bromofluorobenzene	95	174,176
Dibromofluoromethane	113	
Toluene-d_8	98	
Pentafluorobenzene	168	
1,4-Difluorobenzene	114	
Chlorobenzene-d_5	117	
1,4-Dichlorobenzene-d_4	152	

TABLE 6.
VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES
ASSIGNED FOR QUANTITATION

Pentafluorobenzene	1,4-Difluorobenzene
Acetone	Benzene
Acrolein	Bromodichloromethane
Acrylonitrile	Bromofluorobenzene (surrogate)
Bromochloromethane	Carbon tetrachloride
Bromomethane	2-Chloroethyl vinyl ether
2-Butanone	1,2-Dibromoethane
Carbon disulfide	Dibromomethane
Chloroethane	1,2-Dichloroethane
Chloroform	1,2-Dichloroethane-d_4 (surrogate)
Chloromethane	1,2-Dichloropropane
Dichlorodifluoromethane	1,1-Dichloropropene
1,1-Dichloroethane	cis-1,3-Dichloropropene
1,1-Dichloroethene	trans-1,3-Dichloropropene
cis-1,2-Dichloroethene	4-Methyl-2-pentanone
trans-1,2-Dichloroethene	Toluene
2,2-Dichloropropane	Toluene-d_8 (surrogate)
Iodomethane	1,1,2-Trichloroethane
Methylene chloride	Trichloroethene
1,1,1-Trichloroethane	
Trichlorofluoromethane	1,4-Dichlorobenzene-d_4
Vinyl acetate	
Vinyl chloride	Bromobenzene
	n-Butylbenzene
Chlorobenzene-d_5	sec-Butylbenzene
	tert-Butylbenzene
Bromoform	2-Chlorotoluene
Chlorodibromomethane	4-Chlorotoluene
Chlorobenzene	1,2-Dibromo-3-chloropropane
1,3-Dichloropropane	1,2-Dichlorobenzene
Ethylbenzene	1,3-Dichlorobenzene
2-Hexanone	1,4-Dichlorobenzene
Styrene	Hexachlorobutadiene
1,1,1,2-Tetrachloroethane	Isopropyl benzene
Tetrachloroethene	p-Isopropyltoluene
Xylene	Naphthalene
	n-Propylbenzene
	1,1,2,2-Tetrachloroethane
	1,2,3-Trichlorobenzene
	1,2,4-Trichlorobenzene
	1,2,3-Trichloropropane
	1,2,4-Trimethylbenzene
	1,3,5-Trimethylbenzene

TABLE 7.
SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A WIDE-BORE CAPILLARY COLUMN

Analyte	Conc. Range, ug/L	Number of Samples	Recovery,[a] %	Standard Deviation of Recovery[b]	Percent Rel. Std. Dev.
Benzene	0.1 - 10	31	97	6.5	5.7
Bromobenzene	0.1 - 10	30	100	5.5	5.5
Bromochloromethane	0.5 - 10	24	90	5.7	6.4
Bromodichloromethane	0.1 - 10	30	95	5.7	6.1
Bromoform	0.5 - 10	18	101	6.4	6.3
Bromomethane	0.5 - 10	18	95	7.8	8.2
n-Butylbenzene	0.5 - 10	18	100	7.6	7.6
sec-Butylbenzene	0.5 - 10	16	100	7.6	7.6
tert-Butylbenzene	0.5 - 10	18	102	7.4	7.3
Carbon tetrachloride	0.5 - 10	24	84	7.4	8.8
Chlorobenzene	0.1 - 10	31	98	5.8	5.9
Chloroethane	0.5 - 10	24	89	8.0	9.0
Chloroform	0.5 - 10	24	90	5.5	6.1
Chloromethane	0.5 - 10	23	93	8.3	8.9
2-Chlorotoluene	0.1 - 10	31	90	5.6	6.2
4-Chlorotoluene	0.1 - 10	31	99	8.2	8.3
1,2-Dibromo-3-chloropropane	0.5 - 10	24	83	16.6	19.9
Dibromochloromethane	0.1 - 10	31	92	6.5	7.0
1,2-Dibromoethane	0.5 - 10	24	102	4.0	3.9
Dibromomethane	0.5 - 10	24	100	5.6	5.6
1,2-Dichlorobenzene	0.1 - 10	31	93	5.8	6.2
1,3-Dichlorobenzene	0.5 - 10	24	99	6.8	6.9
1,4-Dichlorobenzene	0.2 - 20	31	103	6.6	6.4
Dichlorodifluoromethane	0.5 - 10	18	90	6.9	7.7
1,1-Dichlorobenzene	0.5 - 10	24	96	5.1	5.3
1,2-Dichlorobenzene	0.1 - 10	31	95	5.1	5.4
1,1-Dichloroethene	0.1 - 10	34	94	6.3	6.7
cis-1,2-Dichloroethene	0.5 - 10	18	101	6.7	6.7
trans-1,2-Dichloroethene	0.1 - 10	30	93	5.2	5.6
1,2-Dichloropropane	0.1 - 10	30	97	5.9	6.1
1,3-Dichloropropane	0.1 - 10	31	96	5.7	6.0
2,2-Dichloropropane	0.5 - 10	12	86	14.6	16.9
1,1-Dichloropropene	0.5 - 10	18	98	8.7	8.9
Ethylbenzene	0.1 - 10	31	99	8.4	8.6
Hexachlorobutadiene	0.5 - 10	18	100	6.8	6.8
Isopropylbenzene	0.5 - 10	16	101	7.7	7.6
p-Isopropyltoluene	0.1 - 10	23	99	6.7	6.7

TABLE 7.
(Continued)

Analyte	Conc. Range, ug/L	Number of Samples	Recovery,[a] %	Standard Deviation of Recovery[b]	Percent Rel. Std. Dev.
Methylene chloride	0.1 - 10	30	95	5.0	5.3
Naphthalene	0.1 -100	31	104	8.6	8.2
n-Propylbenzene	0.1 - 10	31	100	5.8	5.8
Styrene	0.1 -100	39	102	7.3	7.2
1,1,1,2-Tetrachloroethane	0.5 - 10	24	90	6.1	6.8
1,1,2,2-Tetrachloroethane	0.1 - 10	30	91	5.7	6.3
Tetrachloroethene	0.5 - 10	24	89	6.0	6.8
Toluene	0.5 - 10	18	102	8.1	8.0
1,2,3-Trichlorobenzene	0.5 - 10	18	109	9.4	8.6
1,2,4-Trichlorobenzene	0.5 - 10	18	108	9.0	8.3
1,1,1-Trichloroethane	0.5 - 10	18	98	7.9	8.1
1,1,2-Trichloroethane	0.5 - 10	18	104	7.6	7.3
Trichloroethene	0.5 - 10	24	90	6.5	7.3
Trichlorofluoromethane	0.5 - 10	24	89	7.2	8.1
1,2,3-Trichloropropane	0.5 - 10	16	108	15.6	14.4
1,2,4-Trimethylbenzene	0.5 - 10	18	99	8.0	8.1
1,3,5-Trimethylbenzene	0.5 - 10	23	92	6.8	7.4
Vinyl chloride	0.5 - 10	18	98	6.5	6.7
o-Xylene	0.1 - 31	18	103	7.4	7.2
m-Xylene	0.1 - 10	31	97	6.3	6.5
p-Xylene	0.5 - 10	18	104	8.0	7.7

[a]Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

[b]Standard deviation was calculated by pooling data form three levels.

TABLE 8.
SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR
VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED
WITH A NARROW BORE CAPILLARY COLUMN

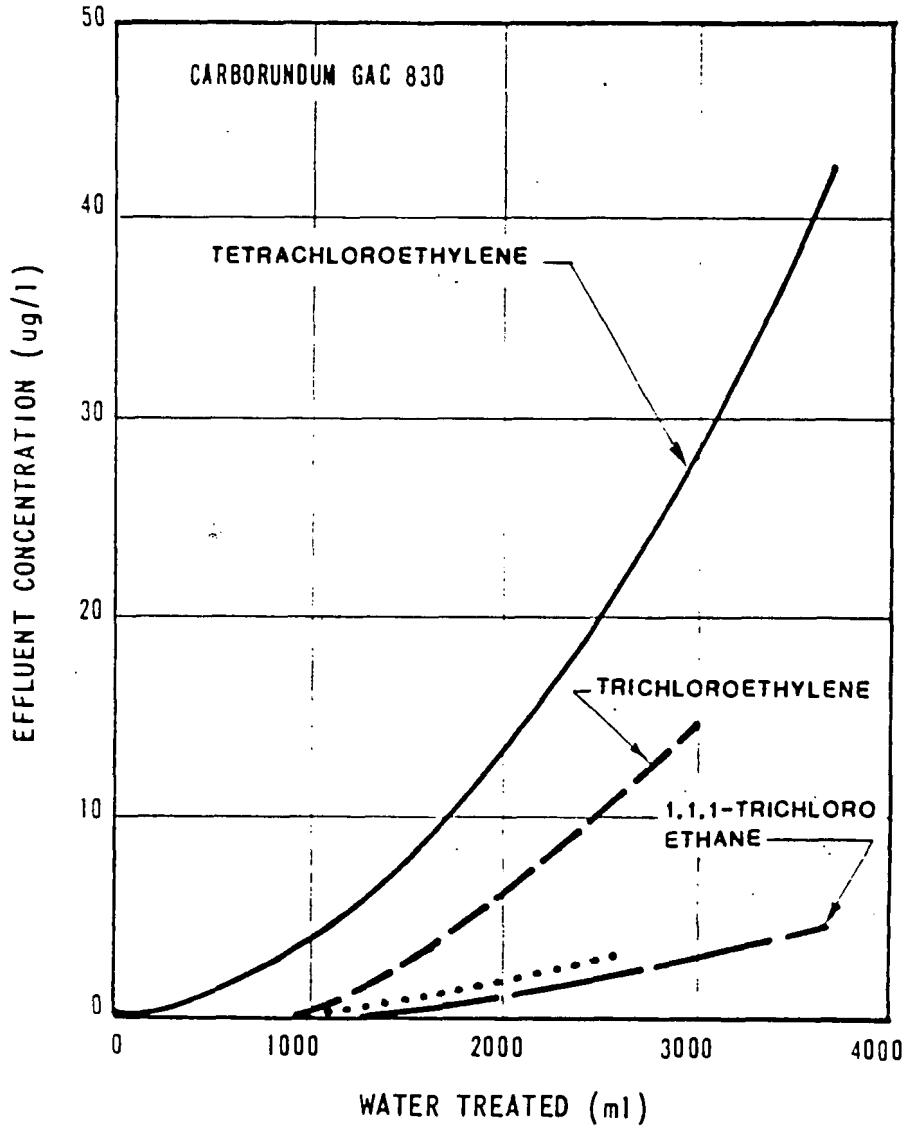
Analyte	Conc. ug/L	Number of Samples	Recovery,[a] %	Standard Deviation of Recovery[b]	Percent Rel. Std. Dev.
Benzene	0.1	7	99	6.2	6.3
Bromobenzene	0.5	7	97	7.4	7.6
Bromochloromethane	0.5	7	97	5.8	6.0
Bromodichloromethane	0.1	7	100	4.6	4.6
Bromoform	0.5	7	101	5.4	5.3
Bromomethane	0.5	7	99	7.1	7.2
n-Butylbenzene	0.5	7	94	6.0	6.4
sec-Butylbenzene	0.5	7	110	7.1	6.5
tert-Butylbenzene	0.5	7	110	2.5	2.3
Carbon tetrachloride	0.1	7	108	6.8	6.3
Chlorobenzene	0.1	7	91	5.8	6.4
Chloroethane	0.1	7	100	5.8	5.8
Chloroform	0.1	7	105	3.2	3.0
Chloromethane	0.5	7	101	4.7	4.7
2-Chlorotoluene	0.5	7	99	4.6	4.6
4-Chlorotoluene	0.5	7	96	7.0	7.3
1,2-Dibromo-3-chloropropane	0.5	7	92	10.0	10.9
Dibromochloromethane	0.1	7	99	5.6	5.7
1,2-Dibromoethane	0.5	7	97	5.6	5.8
Dibromomethane	0.5	7	93	5.6	6.0
1,2-Dichlorobenzene	0.1	7	97	3.5	3.6
1,3-Dichlorobenzene	0.1	7	101	6.0	5.9
1,4-Dichlorobenzene	0.1	7	106	6.5	6.1
Dichlorodifluoromethane	0.1	7	99	8.8	8.9
1,1-Dichloroethane	0.5	7	98	6.2	6.3
1,2-Dichloroethane	0.1	7	100	6.3	6.3
1,1-Dichloroethene	0.1	7	95	9.0	9.5
cis-1,2-Dichloroethene	0.1	7	100	3.7	3.7
trans-1,2-Dichloroethene	0.1	7	98	7.2	7.3
1,2-Dichloropropane	0.5	7	96	6.0	6.3
1,3-Dichloropropane	0.5	7	99	5.8	5.9
2,2-Dichloropropane	0.5	7	99	4.9	4.9
1,1-Dichloropropene	0.5	7	102	7.4	7.3
Ethylbenzene	0.5	7	99	5.2	5.3
Hexachlorobutadiene	0.5	7	100	6.7	6.7
Isopropylbenzene	0.5	7	102	6.4	6.3
p-Isopropyltoluene	0.5	7	113	13.0	11.5

TABLE 8.
(Continued)

Analyte	Conc. ug/L	Number of Samples	Recovery,[a] %	Standard Deviation of Recovery[b]	Percent Rel. Std. Dev.
Methylene chloride	0.5	7	97	13.0	13.4
Naphthalene	0.5	7	98	7.2	7.3
n-Propylbenzene	0.5	7	99	6.6	6.7
Styrene	0.5	7	96	19.0	19.8
1,1,1,2-Tetrachloroethane	0.5	7	100	4.7	4.7
1,1,2,2-Tetrachloroethane	0.5	7	100	12.0	12.0
Tetrachloroethene	0.1	7	96	5.0	5.2
Toluene	0.5	7	100	5.9	5.9
1,2,3-Trichlorobenzene	0.5	7	102	8.9	8.7
1,2,4-Trichlorobenzene	0.5	7	91	16.0	17.6
1,1,1-Trichloroethane	0.5	7	100	4.0	4.0
1,1,2-Trichloroethane	0.5	7	102	4.9	4.8
Trichloroethene	0.1	7	104	2.0	1.9
Trichlorofluoromethane	0.1	7	97	4.6	4.7
1,2,3-Trichloropropane	0.5	7	96	6.5	6.8
1,2,4-Trimethylbenzene	0.5	7	96	6.5	6.8
1,3,5-Trimethylbenzene	0.5	7	101	4.2	4.2
Vinyl chloride	0.1	7	104	0.2	0.2
o-Xylene	0.5	7	106	7.5	7.1
m-Xylene	0.5	7	106	4.6	4.3
p-Xylene	0.5	7	97	6.1	6.3

[a]Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

MINI-COLUMN TEST RESULTS



Define:

- Controlling VOC

- Carbon Usage based on:

$$\text{Carbon usage (lbs/1,000 gal)} = \frac{W}{V} \times 8461.5$$

where W = weight of carbon (0.1 gm)
V = volume treated (ml)

- Preliminary Process Design

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TABLE 9.
SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/Medium Water	Low/Medium Soil/Sediment
4-Bromofluorobenzene[a]	86-115	74-121
Dibromofluoromethane[a]	86-118	80-120
Toluene-d_8[a]	88-110	81-117

[a]Single laboratory data for guidance only.

METHOD 8270

GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR SEMIVOLATILE ORGANICS: CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and ground water. Direct injection of a sample may be used in limited applications.

1.2 Method 8270 can be used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system.

1.3 The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration. Also, chromatography is poor. Under the alkaline conditions of the extraction step, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4 The practical quantitation limit (PQL) of Method 8270 for determining an individual compound is approximately 1 mg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 ug/L for ground water samples (see Table 2). PQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

TABLE 1. CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Acenaphthene	15.13	154	153, 152
Acenaphthene-d_{10} (I.S.)	15.05	164	162, 160
Acenaphthylene	14.57	152	151, 153
Acetophenone	7.96[a]	105	77, 51
Aldrin	--	66	263, 220
Aniline	5.68	93	66, 65
Anthracene	19.77	178	176, 179
4-Aminobiphenyl	19.18[a]	169	168, 170
Aroclor-1016	--	222	260, 292
Aroclor-1221	--	190	224, 260
Aroclor-1232	--	190	224, 260
Aroclor-1242	--	222	256, 292
Aroclor-1248	--	292	362, 326
Aroclor-1254	--	292	362, 326
Aroclor-1260	--	360	362, 394
Benzidine	23.87	184	92, 185
Benzoic acid	9.38	122	105, 77
Benzo(a)anthracene	27.83	228	229, 226
Benzo(b)fluoranthene	31.45	252	253, 125
Benzo(k)fluoranthene	31.55	252	253, 125
Benzo(g,h,i)perylene	41.43	276	138, 277
Benzo(a)pyrene	32.80	252	253, 125
Benzyl alcohol	6.78	108	79, 77
α-BHC	--	183	181, 109
β-BHC	--	181	183, 109
δ-BHC	--	183	181, 109
γ-BHC (Lindane)	--	183	181, 109
Bis(2-chloroethoxy)methane	9.23	93	95, 123
Bis(2-chloroethyl)ether	5.82	93	63, 95
Bis(2-chloroisopropyl)ether	7.22	45	77, 121
Bis(2-ethylhexyl)phthalate	28.47	149	167, 279
4-Bromophenyl phenyl ether	18.27	248	250, 141
Butyl benzyl phthalate	26.43	149	91, 206
Chlordane	--	373	375, 377
4-Chloroaniline	10.08	127	129
1-Chloronaphthalene	13.65[a]	162	127, 164
2-Chloronaphthalene	13.30	162	127, 164
4-Chloro-3-methylphenol	11.68	107	144, 142
2-Chlorophenol	5.97	128	64, 130
4-Chlorophenyl phenyl ether	16.78	204	206, 141
Chrysene	27.97	228	226, 229
Chrysene-d_{12} (I.S.)	27.88	240	120, 236
4,4'-DDD	--	235	237, 165
4,4'-DDE	--	246	248, 176

TABLE 1. CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS (Continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
4,4'-DDT	--	235	237, 165
Dibenz(a,j)acridine	32.55[a]	279	280, 277
Dibenz(a,h)anthracene	39.82	278	139, 279
Dibenzofuran	15.63	168	139
Di-n-butylphthalate	21.78	149	150, 104
1,3-Dichlorobenzene	6.27	146	148, 111
1,4-Dichlorobenzene	6.40	146	148, 111
1,4-Dichlorobenzene-d_4 (I.S.)	6.35	152	150, 115
1,2-Dichlorobenzene	6.85	146	148, 111
3,3'-Dichlorobenzidine	27.88	252	254, 126
2,4-Dichlorophenol	9.48	162	164, 98
2,6-Dichlorophenol	10.05[a]	162	164, 98
Dieldrin	--	79	263, 279
Diethylphthalate	16.70	149	177, 150
p-Dimethylaminoazobenzene	24.48[a]	120	225, 77
7,12-Dimethylbenz(a)anthracene	29.54[a]	256	241, 257
α-,α-Dimethylphenethylamine	9.51[a]	58	91, 42
2,4-Dimethylphenol	9.03	122	107, 121
Dimethylphthalate	14.48	163	194, 164
4,6-Dinitro-2-methylphenol	17.05	198	51, 105
2,4-Dinitrophenol	15.35	184	63, 154
2,4-Dinitrotoluene	15.80	165	63, 89
2,6-Dinitrotoluene	14.62	165	63, 89
Diphenylamine	17.54[a]	169	168, 167
1,2-Diphenylhydrazine	--	77	105, 182
Di-n-octylphthalate	30.48	149	167, 43
Endosulfan I	--	195	339, 341
Endosulfan II	--	337	339, 341
Endosulfan sulfate	--	272	387, 422
Endrin	--	263	82, 81
Endrin aldehyde	--	67	345, 250
Endrin ketone	--	317	67, 319
Ethyl methanesulfonate	5.33[a]	79	109, 97
Fluoranthene	23.33	202	101, 203
Fluorene	16.70	166	165, 167
2-Fluorobiphenyl (surr.)	--	172	171
2-Fluorophenol (surr.)	--	112	64
Heptachlor	--	100	272, 274
Heptachlor epoxide	--	353	355, 351
Hexachlorobenzene	18.65	284	142, 249
Hexachlorobutadiene	10.43	225	223, 227
Hexachlorocyclopentadiene	12.60	237	235, 272
Hexachloroethane	7.65	117	201, 199
Indeno(1,2,3-cd)pyrene	39.52	276	138, 227

TABLE 1. CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS (Continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Isophorone	8.53	82	95, 138
Methoxychlor	--	227	228
3-Methylcholanthrene	31.14[a]	268	253, 267
Methyl methanesulfonate	4.32[a]	80	79, 65
2-Methylnaphthalene	11.87	142	141
2-Methylphenol (o-cresol)	7.22	108	107, 79
4-Methylphenol (p-cresol)	7.60	108	107, 79
Naphthalene	9.82	128	129, 127
Naphthalene-d_8 (I.S.)	9.75	136	68
1-Naphthylamine	15.80[a]	143	115, 116
2-Naphthylamine	16.00[a]	143	115, 116
2-Nitroaniline	13.75	65	92, 138
3-Nitroaniline	15.02	138	108, 92
4-Nitroaniline	16.90	138	108, 92
Nitrobenzene	7.87	77	123, 65
Nitrobenzene-d_5 (surr.)	--	82	128, 54
2-Nitrophenol	8.75	139	109, 65
4-Nitrophenol	15.80	139	109, 65
N-Nitroso-di-n-butylamine	10.99[a]	84	57, 41
N-Nitrosodimethylamine	--	42	74, 44
N-Nitrosodiphenylamine	17.17	169	168, 167
N-Nitrosodipropylamine	7.55	70	42, 101, 130
N-Nitrosopiperidine	--	42	114, 55
Pentachlorobenzene	15.64[a]	250	252, 248
Pentachloronitrobenzene	19.47[a]	295	237, 142
Pentachlorophenol	19.25	266	264, 268
Perylene-d_{12} (I.S.)	33.05	264	260, 265
Phenacetin	18.59[a]	108	109, 179
Phenanthrene	19.62	178	179, 176
Phenanthrene-d_{10} (I.S.)	19.55	188	94, 80
Phenol	5.77	94	65, 66
Phenol-d_6 (surr.)	--	99	42, 71
2-Picoline	3.75[a]	93	66, 92
Pronamide	19.61[a]	173	175, 145
Pyrene	24.02	202	200, 203
Terphenyl-d_{14} (surr.)	--	244	122, 212
1,2,4,5-Tetrachlorobenzene	13.62[a]	216	214, 218
2,3,4,6-Tetrachlorophenol	16.09[a]	232	230, 131
2,4,6-Tribromophenol (surr.)	--	330	332, 141
1,2,4-Trichlorobenzene	9.67	180	182, 145
2,4,5-Trichlorophenol	13.00	196	198, 200
2,4,6-Trichlorophenol	12.85	196	198, 200
Toxaphene	--	159	231, 233

I.S. = internal standard
surr. = surrogate

[a]Estimated retention times.

TABLE 2. PRACTICAL QUANTITATION LIMITS (PQL) FOR SEMIVOLATILE ORGANICS**

Semivolatiles	CAS Number	Practical Quantitation Limits*	
		Ground Water	Low Soil/Sediment[1]
		ug/L	ug/Kg
Phenol	108-95-2	10	660
bis(2-Chloroethyl) ether	111-44-4	10	660
2-Chlorophenol	95-57-8	10	660
1,3-Dichlorobenzene	541-73-1	10	660
1,4-Dichlorobenzene	106-46-7	10	660
Benzyl Alcohol	100-51-6	20	1300
1,2-Dichlorobenzene	95-50-1	10	660
2-Methylphenol	95-48-7	10	660
bis(2-Chloroisopropyl) ether	39638-32-9	10	660
4-Methylphenol	106-44-5	10	660
N-Nitroso-Di-N-propylamine	621-64-7	10	660
Hexachloroethane	67-72-1	10	660
Nitrobenzene	98-95-3	10	660
Isophorone	78-59-1	10	660
2-Nitrophenol	88-75-5	10	660
2,4-Dimethylphenol	105-67-9	10	660
Benzoic Acid	65-85-0	50	3300
bis(2-Chloroethoxy) methane	111-91-1	10	660
2,4-Dichlorophenol	120-83-2	10	660
1,2,4-Trichlorobenzene	120-82-1	10	660
Naphthalene	91-20-3	10	660
4-Chloroaniline	106-47-8	20	1300
Hexachlorobutadiene	87-68-3	10	660
4-Chloro-3-methylphenol	59-50-7	20	1300
2-Methylnaphthalene	91-57-6	10	660
Hexachlorocyclopentadiene	77-47-4	10	660
2,4,6-Trichlorophenol	88-06-2	10	660
2,4,5-Trichlorophenol	95-95-4	10	660

TABLE 2. PRACTICAL QUANTITATION LIMITS (PQL) FOR SEMIVOLATILE ORGANICS** (Continued)

Semivolatiles	CAS Number	Practical Quantitation Limits*	
		Ground Water	Low Soil/Sediment[1]
		ug/L	ug/Kg
2-Chloronaphthalene	91-58-7	10	660
2-Nitroaniline	88-74-4	50	3300
Dimethyl phthalate	131-11-3	10	660
Acenaphthylene	208-96-8	10	660
3-Nitroaniline	99-09-2	50	3300
Acenaphthene	83-32-9	10	660
2,4-Dinitrophenol	51-28-5	50	3300
4-Nitrophenol	100-02-7	50	3300
Dibenzofuran	132-64-9	10	660
2,4-Dinitrotoluene	121-14-2	10	660
2,6-Dinitrotoluene	606-20-2	10	660
Diethylphthalate	84-66-2	10	660
4-Chlorophenyl phenyl ether	7005-72-3	10	660
Fluorene	86-73-7	10	660
4-Nitroaniline	100-01-6	50	3300
4,6-Dinitro-2-methylphenol	534-52-1	50	3300
N-Nitrosodiphenylamine	86-30-6	10	660
4-Bromophenyl phenyl ether	101-55-3	10	660
Hexachlorobenzene	118-74-1	10	660
Pentachlorophenol	87-86-5	50	3300
Phenanthrene	85-01-8	10	660
Anthracene	120-12-7	10	660
Di-n-butylphthalate	84-74-2	10	660
Fluoranthene	206-44-0	10	660
Pyrene	129-00-0	10	660
Butyl benzyl phthalate	85-68-7	10	660
3,3'-Dichlorobenzidine	91-94-1	20	1300
Benzo(a)anthracene	56-55-3	10	660
bis(2-ethylhexyl)phthalate	117-81-7	10	660

TABLE 2. PRACTICAL QUANTITATION LIMITS (PQL) FOR SEMIVOLATILE ORGANICS** (Continued)

Semi-Volatiles	CAS Number	Practical Quantitation Limits*	
		Ground Water	Low Soil/Sediment[1]
		ug/L	ug/Kg
Chrysene	218-01-9	10	660
Di-n-octyl phthalate	117-84-0	10	660
Benzo(b)fluoranthene	205-99-2	10	660
Benzo(k)fluoranthene	207-08-9	10	660
Benzo(a)pyrene	50-32-8	10	660
Indeno(1,2,3-cd)pyrene	193-39-5	10	660
Dibenz(a,h)anthracene	53-70-3	10	660
Benzo(g,h,i)perylene	191-24-2	10	660

*PQLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis, therefore, PQLs will be higher based on the % moisture in each sample. This is based on a 30-g sample and gel permeation chromatography cleanup.

**Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achieveable.

Other Matrices	Factor[1]
Medium-level soil and sludges by sonicator	7.5
Non-water-miscible waste	75

[1]PQL = [PQL for Ground Water (Table 2)] X [Factor].

2.0 SUMMARY OF METHOD

2.1 Prior to using this method, the samples should be prepared for chromatography using the appropriate sample preparation and cleanup methods. This method describes chromatographic conditions that will allow for the separation of the compounds in the extract.

3.0 INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

3.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph/mass spectrometer system:

4.1.1 **Gas chromatograph:** An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

4.1.2 **Column:** 30-m x 0.25-mm I.D. (or 0.32-mm I.D.) 1-um film thickness silicon-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent).

4.1.3 **Mass spectrometer:** Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 3 when 1 uL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

4.1.4 **GC/MS interface:** Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be used.

4.1.5 **Data system:** A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have

TABLE 3. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA[a]

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40-60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	>1% of mass 198
441	Present but less than mass 443
442	>40% of mass 198
443	17-23% of mass 442

[a]J.W. Eichelberger, L.E. Harris, and W.L. Budde. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry", Analytical Chemistry, 47, 995 (1975).

software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library should also be available.

4.2 Syringe: 10-uL.

5.0 REAGENTS

5.1 Stock standard solutions (1.00 ug/uL): Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.1.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.1.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.1.3 Stock standard solutions must be replaced after 1 yr or sooner if comparison with quality control check samples indicates a problem.

5.2 Internal standard solutions: The internal standards recommended are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. Other compounds may be used as internal standards as long as the requirements given in Paragraph 7.3.2 are met. Dissolve 200 mg of each compound with a small volume of carbon disulfide. Transfer to a 50-mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is approximately 20% carbon disulfide. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. The resulting solution will contain each standard at a concentration of 4,000 ng/uL. Each 1-mL sample extract undergoing analysis should be spiked with 10 uL of the internal standard solution, resulting in a concentration of 40 ng/uL of each internal standard. Store at 4°C or less when not being used.

5.3 GC/MS tuning standard: A methylene chloride solution containing 50 ng/uL of decafluorotriphenylphosphine (DFTPP) should be prepared. The

standard should also contain 50 ng/uL each of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Store at 4°C or less when not being used.

5.4 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared. One of the calibration standards should be at a concentration near, but above, the method detection limit; the others should correspond to the range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method (e.g., some or all of the compounds listed in Table 1 may be included). Each 1-mL aliquot of calibration standard should be spiked with 10 uL of the internal standard solution prior to analysis. All standards should be stored at -10°C to -20°C and should be freshly prepared once a year, or sooner if check standards indicate a problem. The daily calibration standard should be prepared weekly and stored at 4°C.

5.5 Surrogate standards: The recommended surrogate standards are phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. See Method 3500 for the instructions on preparing the surrogate standards. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all blanks, spikes, and sample extracts. Take into account all dilutions of sample extracts.

5.6 Matrix spike standards: See Method 3500 for instructions on preparing the matrix spike standard. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all blanks, spikes, and sample extracts. Take into account all dilutions of sample extracts.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sample preparation: Samples must be prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Water	3510, 3520
Soil/sediment	3540, 3550
Waste	3540, 3550, 3580

7.1.1 **Direct injection:** In very limited applications direct injection of the sample into the GC/MS system with a 10 uL syringe may be appropriate. The detection limit is very high (approximately 10,000 ug/L); therefore, it is only permitted where concentrations in excess of 10,000 ug/L are expected. The system must be calibrated by direct injection.

7.2 Extract cleanup: Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Compounds	Methods
Phenols	3630, 3640, 8040[a]
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3620, 3640, 3660
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorous pesticides	3620, 3640
Petroleum waste	3611, 3650
All priority pollutant base, neutral, and acids	3640

[a]Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered on GC/FID.

7.3 Initial calibration: The recommended GC/MS operating conditions:

Mass range: 35-500 amu
Scan time: 1 sec/scan
Initial column temperature and hold time: 40°C for 4 min
Column temperature program: 40-270°C at 10°C/min
Final column temperature hold: 270°C (until benzo[g,h,i]perylene has eluted)
Injector temperature: 250-300°C
Transfer line temperature: 250-300°C
Source temperature: According to manufacturer's specifications
Injector: Grob-type, splitless
Sample volume: 1-2 uL
Carrier gas: Hydrogen at 50 cm/sec or helium at 30 cm/sec.

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 3 for a 50-ng injection of DFTPP. Analyses should not begin until all these criteria are met. Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6-12 in. of the capillary column.

7.3.2 The internal standards selected in Paragraph 5.1 should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion, i.e., for 1,4-dichlorobenzene-d_4 use m/z 152 for quantitation.

7.3.3 Analyze 1 uL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (as indicated in Table 1). Figure 1 shows a chromatogram of a calibration standard containing base/neutral and acid analytes. Calculate response factors (RFs) for each compound as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$

where:

A_x = Area of the characteristic ion for the compound being measured.

A_{is} = Area of the characteristic ion for the specific internal standard.

C_x = Concentration of the compound being measured (ng/uL).

C_{is} = Concentration of the specific internal standard (ng/uL).

7.3.4 The average RF should be calculated for each compound. The percent relative standard deviation (%RSD = 100[SD/$\overline{RF}$]) should also be calculated for each compound. The %RSD should be less than 30% for each compound. However, the %RSD for each individual Calibration Check Compound (CCC) (see Table 4) must be less than 30%. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

7.3.5 A system performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-nitroso-di-n-propylamine; hexachlorocyclopentadiene; 2,4-dinitrophenol; and 4-nitrophenol. The minimum acceptable average $\overline{RF}$ for these compounds SPCCs is 0.050. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

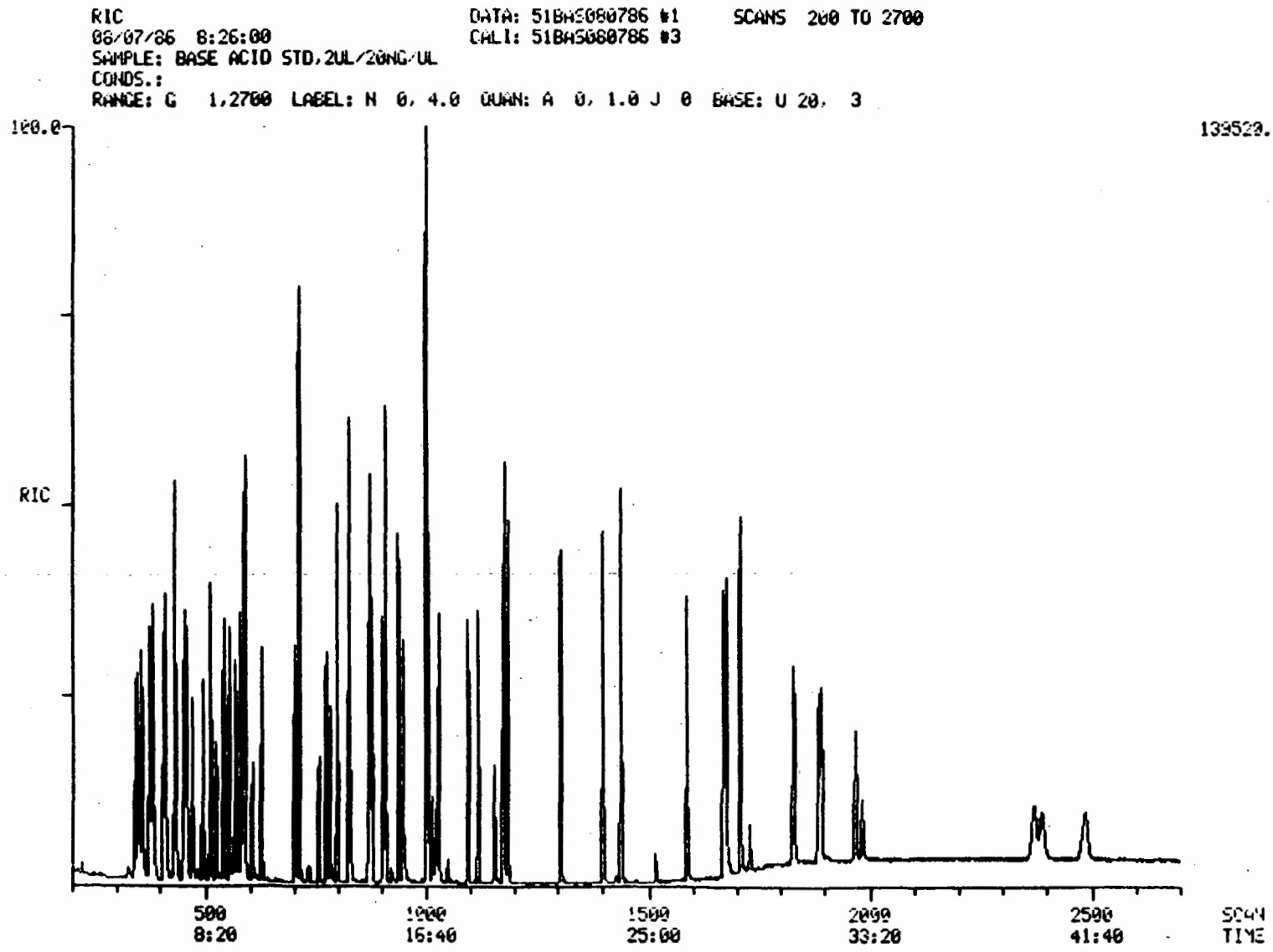


Figure 1. Gas chromatogram of base/neutral and acid calibration standard.

TABLE 4. CALIBRATION CHECK COMPOUNDS

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitroso-di-n-phenylamine	Phenol
Di-n-octylphthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

7.4 Daily GC/MS calibration:

7.4.1 Prior to analysis of samples, the GC/MS tuning standard must be analyzed. A 50-ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 3. These criteria must be demonstrated during each 12-hr shift.

7.4.2 A calibration standard(s) at mid-level concentration containing all semivolatile analytes, including all required surrogates, must be performed every 12-hr during analysis. Compare the response factor data from the standards every 12-hr with the average response factor from the initial calibration for a specific instrument as per the SPCC (Paragraph 7.4.3) and CCC (Paragraph 7.4.4) criteria.

7.4.3 **System Performance Check Compounds** (SPCCs): A system performance check must be made during every 12 hr shift. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum RF for semivolatile SPCCs is 0.050. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins.

7.4.4 **Calibration Check Compounds** (CCCs): After the system performance check is met, CCCs listed in Table 4 are used to check the validity of the initial calibration. Calculate the percent difference using:

$$\% \text{ Difference} = \frac{\overline{RF}_I - RF_C}{\overline{RF}_I} \times 100$$

where:

$\overline{RF}_I$ = average response factor from initial calibration.

RF_C = response factor from current verification check standard.

If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than 30%, the initial calibration is assumed to be valid. If the criterion is not met (>30% difference) for any one CCC, corrective action MUST be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration MUST be generated. This criterion MUST be met before sample analysis begins.

7.4.5 The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 sec from the last check calibration (12 hr), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

7.5 GC/MS analysis:

7.5.1 It is highly recommended that the extract be screened on a GC/FID or GC/PID using the same type of capillary column. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

7.5.2 Spike the 1-mL extract obtained from sample preparation with 10 uL of the internal standard solution just prior to analysis.

7.5.3 Analyze the 1-mL extract by GC/MS using a 30-m x 0.25-mm (or 0.32-mm) silicone-coated fused-silica capillary column. The volume to be injected should ideally contain 100 ng of base/neutral and 200 ng of acid surrogates (for a 1 uL injection). The recommended GC/MS operating conditions to be used are specified in Paragraph 7.3.

7.5.4 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 40 ng/uL of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

7.5.5 Perform all qualitative and quantitative measurements as described in Paragraph 7.6. Store the extracts at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

7.6 Data interpretation:

7.6.1 **Qualitative analysis:**

7.6.1.1 An analyte (e.g., those listed in Table 1) is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference should be obtained on the user's GC/MS within the same 12 hours as the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as the standard component; and (2) correspondence of the sample component and the standard component mass spectrum.

7.6.1.1.1 The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hrs as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

7.6.1.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100% must be present in the sample spectrum.

7.6.1.1.3 The relative intensities of ions specified in Paragraph 7.6.1.1.2 must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.

7.6.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in sample the spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.6.2 **Quantitative analysis:**

7.6.2.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (e.g., see Table 5).

7.6.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water:

$$\text{concentration (ug/L)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_o)(V_i)}$$

where:

A_x = Area of characteristic ion for compound being measured.

I_s = Amount of internal standard injected (ng).

V_t = Volume of total extract, taking into account dilutions (i.e., a 1-to-10 dilution of a 1-mL extract will mean V_t = 10,000 uL. If half the base/neutral extract and half the acid extract are combined, V_t = 2,000.

A_{is} = Area of characteristic ion for the internal standard.

RF = Response factor for compound being measured (Paragraph 7.3.3).

V_o = Volume of water extracted (mL).

V_i = Volume of extract injected (uL).

Sediment/Soil Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis):

$$\text{concentration (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)(D)}$$

where:

A_x, I_s, V_t, A_{is}, RF, V_i = same as for water.

W_s = weight of sample extracted or diluted in grams.

D = (100 - % moisture in sample)/100, or 1 for a wet-weight basis.

TABLE 5. SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl)ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl)ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethyl-phenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr.)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr.)
4-Methylphenol	Nitrobenzene	Hexachlorocyclo-pentadiene
N-Nitrosodimethylamine	Nitrobenzene-d_8 (surr.)	1-Naphthylamine
N-Nitroso-di-n-propylamine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitroso-di-n-butylamine	2-Nitroaniline
Phenol-d_6 (surr.)	N-Nitrosopiperidine	3-Nitroaniline
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetra-chlorobenzene
		2,3,4,6-Tetra-chlorophenol
		2,4,6-Tribromo-phenol (surr.)
		2,4,6-Trichloro-phenol
		2,4,5-Trichloro-phenol

(surr.) = surrogate

TABLE 5. SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION (Continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4-Aminobiphenyl	Benzidine	Benzo(b)fluoranthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl)phthalate	Benzo(g,h,i)perylene
Di-n-butyl phthalate	Butylbenzylphthalate	Benzo(a)pyrene
4,6-Dinitro-2-methylphenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)anthracene
1,2-Diphenylhydrazine	p-Dimethylaminoazobenzene	7,12-Dimethylbenz(a)anthracene
Fluoranthene	Pyrene	Di-n-octylphthalate
Hexachlorobenzene	Terphenyl-d_{14} (surr.)	Indeno(1,2,3-cd)pyrene
N-Nitrosodiphenylamine		3-Methylcholanthrene
Pentachlorophenol		
Pentachloronitrobenzene		
Phenacetin		
Phenanthrene		
Pronamide		

(surr.) = surrogate

7.6.2.3 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulas given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.6.2.4 Report results without correction for recovery data. When duplicates and spiked samples are analyzed, report all data obtained with the sample results.

7.6.2.5 Quantitation of multicomponent compounds (e.g., Aroclors) is beyond the scope of Method 8270. Normally, quantitation is performed using a GC/ECD by Method 8080.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.3 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g, column changed), recalibration of the system must take place.

8.4 Required instrument QC is found in the following sections:

8.4.1 The GC/MS system must be tuned to meet the DFTPP specifications in Section 7.3.1 and 7.4.1.

8.4.2 There must be an initial calibration of the GC/MS system as specified in 7.3.

8.4.3 The GC/MS system must meet the SPCC criteria specified in 7.4.3 and the CCC criteria in 7.4.4, each 12 hr.

8.5 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.5.1 A quality (QC) check sample concentrate is required containing each analyte at a concentration of 100 ug/mL in acetone. The QC check sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC check sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.5.2 Using a pipet, prepare QC check samples at a concentration of 100 ug/L by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.5.3 Analyze the well-mixed QC check samples according to the method beginning in Section 7.1 with extraction of the samples.

8.5.4 Calculate the average recovery ($\bar{X}$) in ug/L, and the standard deviation of the recovery (s) in ug/L, for each analyte of interest using the four results.

8.5.5 For each analyte compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and $\bar{X}$ for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are analyzed.

8.5.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.5.6.1 or 8.5.6.2.

8.5.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Section 8.5.2.

TABLE 6. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range p, p_s (%)
Acenaphthene	100	27.6	60.1-132.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Aldrin	100	39.0	7.2-152.2	D-166
Anthracene	100	32.0	43.4-118.0	27.133
Benzo(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-162
Benzo(a)pyrene	100	39.0	31.7-148.0	17-163
Benzo(ghi)perylene	100	58.9	D-195.0	D-219
Benzyl butyl phthalate	100	23.4	D-139.9	D-152
β-BHC	100	31.5	41.5-130.6	24-149
δ-BHC	100	21.6	D-100.0	D-110
Bis(2-chloroethyl)ether	100	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl)ether	100	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl)phthalate	100	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4	53-127
2-Chloronaphthalene	100	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158
Chrysene	100	48.3	44.1-139.9	17-168
4,4'-DDD	100	31.0	D-134.5	D-145
4,4'-DDE	100	32.0	19.2-119.7	4-136
4,4'-DDT	100	61.6	D-170.6	D-203
Dibenzo(a,h)anthracene	100	70.0	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3'-Dichlorobenzidine	100	71.4	8.2-212.5	D-262
Dieldrin	100	30.7	44.3-119.3	29-136
Diethyl phthalate	100	26.5	D-100.0	D-114
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
Di-n-octylphthalate	100	31.4	18.6-131.8	4-146
Endosulfan sulfate	100	16.7	D-103.5	D-107
Endrin aldehyde	100	32.5	D-188.8	D-209
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.6-108.4	59-121
Heptachlor	100	37.2	D-172.2	D-192
Heptachlor epoxide	100	54.7	70.9-109.4	26.155
Hexachlorobenzene	100	24.9	7.8-141.5	D-152
Hexachlorobutadiene	100	26.3	37.8-102.2	24-116
Hexachloroethane	100	24.5	55.2-100.0	40-113

TABLE 6. QC ACCEPTANCE CRITERIA[a] - Continued

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range p, p_s (%)
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Isophorone	100	63.3	46.6-180.2	21-196
Naphthalene	100	30.1	35.6-119.6	21-133
Nitrobenzene	100	39.3	54.3-157.6	35-180
N-Nitrosodi-n-propylamine	100	55.4	13.6-197.9	D-230
PCB-1260	100	54.2	19.3-121.0	D-164
Phenanthrene	100	20.6	65.2-108.7	54-120
Pyrene	100	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2	44-142
4-Chloro-3-methylphenol	100	37.2	40.8-127.9	22-147
2-Chlorophenol	100	28.7	36.2-120.4	23-134
2,4-Chlorophenol	100	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	100	26.1	41.8-109.0	32-119
2,4-Dinitrophenol	100	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0-100.0	D-181
2-Nitrophenol	100	35.2	45.0-166.7	29-182
4-Nitrophenol	100	47.2	13.0-106.5	D-132
Pentachlorophenol	100	48.9	38.1-151.8	14-176
Phenol	100	22.6	16.6-100.0	5-112
2,4,6-Trichlorophenol	100	31.7	52.4-129.2	37-144

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

p, p_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 625. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

8.5.6.2 Beginning with Section 8.5.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a reagent blank, a matrix spike, and a matrix spike duplicate/duplicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.6.1 The concentration of the spike in the sample should be determined as follows:

8.6.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in the sample is not being checked against a limit specific to that analyte, the spike should be at 100 ug/L or 1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

8.6.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be at (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 ug/L.

8.6.2 Analyze one sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC check sample concentrate (Section 8.5.1) appropriate for the background concentration in the sample. Spike a second sample aliquot with 1.00 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A-B)%/T, where T is the known true value of the spike.

8.6.3 Compare the percent recovery (p) for each analyte with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 100 ug/L, the analyst must use either the QC acceptance criteria presented in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte:

(1) Calculate accuracy (x') using the equation found in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting x' for $\bar{x}$; (3) calculate the range for recovery at the spike concentration as $(100x'/T) \pm 2.44(100S'/T)\%$.

8.6.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed as described in Section 8.7.

8.7 If any analyte fails the acceptance criteria for recovery in Section 8.6, a QC check standard containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes in Table 6 must be measured in the sample in Section 8.6, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spiked sample.

8.7.1 Prepare the QC check standard by adding 1.0 mL of the QC check sample concentrate (Section 8.5.1 or 8.6.2) to 1 L of reagent water. The QC check standard needs only to contain the analytes that failed criteria in the test in Section 8.6.

8.7.2 Analyzed the QC check standard to determine the concentration measured (A) of each analyte. Calculate each percent recovery (p_s) as 100 (A/T)%, where T is the true value of the standard concentration.

8.7.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in Table 6. Only analytes that failed the test in Section 8.6 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.8 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix) as in Section 8.6, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.9 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Acenaphthene	0.96C+0.19	0.15X-0.12	0.21X-0.67
Acenaphthylene	0.89C+0.74	0.24X-1.06	0.26X-0.54
Aldrin	0.78C+1.66	0.27X-1.28	0.43X+1.13
Anthracene	0.80C+0.68	0.21X-0.32	0.27X-0.64
Benzo(a)anthracene	0.88C-0.60	0.15X+0.93	0.26X-0.21
Chloroethane	0.99C-1.53	0.14X-0.13	0.17X-0.28
Benzo(b)fluoranthene	0.93C-1.80	0.22X+0.43	0.29X+0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19X+1.03	0.35X+0.40
Benzo(a)pyrene	0.90C-0.13	0.22X+0.48	0.32X+1.35
Benzo(ghi)perylene	0.98C-0.86	0.29X+2.40	0.51X-0.44
Benzyl butyl phthalate	0.66C-1.68	0.18X+0.94	0.53X+0.92
β-BHC	0.87C-0.94	0.20X-0.58	0.30X+1.94
δ-BHC	0.29C-1.09	0.34X+0.86	0.93X-0.17
Bis(2-chloroethyl)ether	0.86C-1.54	0.35X-0.99	0.35X+0.10
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16X+1.34	0.26X+2.01
Bis(2-chloroisopropyl)ether	1.03C-2.31	0.24X+0.28	0.25X+1.04
Bis(2-ethylhexyl)phthalate	0.84C-1.18	0.26X+0.73	0.36X+0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13X+0.66	0.16X+0.66
2-Chloronaphthalene	0.89C+0.01	0.07X+0.52	0.13X+0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20X-0.94	0.30X-0.46
Chrysene	0.93C-1.00	0.28X+0.13	0.33X-0.09
4,4'-DDD	0.56C-0.40	0.29X-0.32	0.66X-0.96
4,4'-DDE	0.70C-0.54	0.26X-1.17	0.39X-1.04
4,4'-DDT	0.79C-3.28	0.42X+0.19	0.65X-0.58
Dibenzo(a,h)anthracene	0.88C+4.72	0.30X+8.51	0.59X+0.25
Di-n-butyl phthalate	0.59C+0.71	0.13X+1.16	0.39X+0.60
1,2-Dichlorobenzene	0.80C+0.28	0.20X+0.47	0.24X+0.39
1,3-Dichlorobenzene	0.86C-0.70	0.25X+0.68	0.41X+0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24X+0.23	0.29X+0.36
3,3'-Dichlorobenzidine	1.23C-12.65	0.28X+7.33	0.47X+3.45
Dieldrin	0.82C-0.16	0.20X-0.16	0.26X-0.07
Diethyl phthalate	0.43C+1.00	0.28X+1.44	0.52X+0.22
Dimethyl phthalate	0.20C+1.03	0.54X+0.19	1.05X-0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12X+1.06	0.21X+1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14X+1.26	0.19X+0.35
Di-n-octylphthalate	0.76C-0.79	0.21X+1.19	0.37X+1.19
Endosulfan sulfate	0.39C+0.41	0.12X+2.47	0.63X-1.03
Endrin aldehyde	0.76C-3.86	0.18X+3.91	0.73X-0.62
Fluoranthene	0.81C+1.10	0.22X-0.73	0.28X-0.60
Fluorene	0.90C-0.00	0.12X+0.26	0.13X+0.61
Heptachlor	0.87C-2.97	0.24X-0.56	0.50X-0.23
Heptachlor epoxide	0.92C-1.87	0.33X-0.46	0.28X+0.64
Hexachlorobenzene	0.74C+0.66	0.18X-0.10	0.43X-0.52
Hexachlorobutadiene	0.71C-1.01	0.19X+0.92	0.26X+0.49
Hexachloroethane	0.73C-0.83	0.17X+0.67	0.17X+0.80

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a] - Continued

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Indeno(1,2,3-cd)pyrene	0.78C-3.10	0.29$\bar{X}$+1.46	0.50$\bar{X}$-0.44
Isophorone	1.12C+1.41	0.27$\bar{X}$+0.77	0.33$\bar{X}$+0.26
Naphthalene	0.76C+1.58	0.21$\bar{X}$-0.41	0.30$\bar{X}$-0.68
Nitrobenzene	1.09C-3.05	0.19$\bar{X}$+0.92	0.27$\bar{X}$+0.21
N-Nitrosodi-n-propylamine	1.12C-6.22	0.27$\bar{X}$+0.68	0.44$\bar{X}$+0.47
PCB-1260	0.81C-10.86	0.35$\bar{X}$+3.61	0.43$\bar{X}$+1.82
Phenanthrene	0.87C+0.06	0.12$\bar{X}$+0.57	0.15$\bar{X}$+0.25
Pyrene	0.84C-0.16	0.16$\bar{X}$+0.06	0.15$\bar{X}$+0.31
1,2,4-Trichlorobenzene	0.94C-0.79	0.15$\bar{X}$+0.85	0.21$\bar{X}$+0.39
4-Chloro-3-methylphenol	0.84C+0.35	0.23$\bar{X}$+0.75	0.29$\bar{X}$+1.31
2-Chlorophenol	0.78C+0.29	0.18$\bar{X}$+1.46	0.28$\bar{X}$+0.97
2,4-Dichlorophenol	0.87C-0.13	0.15$\bar{X}$+1.25	0.21$\bar{X}$+1.28
2,4-Dimethylphenol	0.71C+4.41	0.16$\bar{X}$+1.21	0.22$\bar{X}$+1.31
2,4-Dinitrophenol	0.81C-18.04	0.38$\bar{X}$+2.36	0.42$\bar{X}$+26.29
2-Methyl-4,6-dinitrophenol	1.04C-28.04	0.10$\bar{X}$+42.29	0.26$\bar{X}$+23.10
2-Nitrophenol	0.07C-1.15	0.16$\bar{X}$+1.94	0.27$\bar{X}$+2.60
4-Nitrophenol	0.61C-1.22	0.38$\bar{X}$+2.57	0.44$\bar{X}$+3.24
Pentachlorophenol	0.93C+1.99	0.24$\bar{X}$+3.03	0.30$\bar{X}$+4.33
Phenol	0.43C+1.26	0.26$\bar{X}$+0.73	0.35$\bar{X}$+0.58
2,4,6-Trichlorophenol	0.91C-0.18	0.16$\bar{X}$+2.22	0.22$\bar{X}$+1.81

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.

8.9.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.9.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (P) and standard deviation of the percent recovery (s) for each of the surrogates.

8.9.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

$$\text{Upper Control Limit (UCL)} = p + 3s$$
$$\text{Lower Control Limit (LCL)} = p - 3s$$

8.9.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 8. The limits given in Table 8 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Paragraph 8.9.3 must fall within those given in Table 8 for these matrices.

8.9.5 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.9.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

TABLE 8. SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/Medium Water	Low/Medium Soil/Sediment
Nitrobenzene-d_5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
p-Terphenyl-d_{14}	33-141	18-137
Phenol-d_6	10-94	24-113
2-Fluorophenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122

9.0 METHOD PERFORMANCE

9.1 Method 8250 was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-1,300 ug/L. Single operator accuracy and precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act, Method 625," October 26, 1984.

2. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

3. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, 58-63, 1983.

4. Eichelberger, J.W., L.E. Harris, and W.L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems," Analytical Chemistry, 47, 995-1000, 1975.

5. "Method Detection Limit for Methods 624 and 625," Olynyk, P., W.L. Budde, and J.W. Eichelberger, Unpublished report, October 1980.

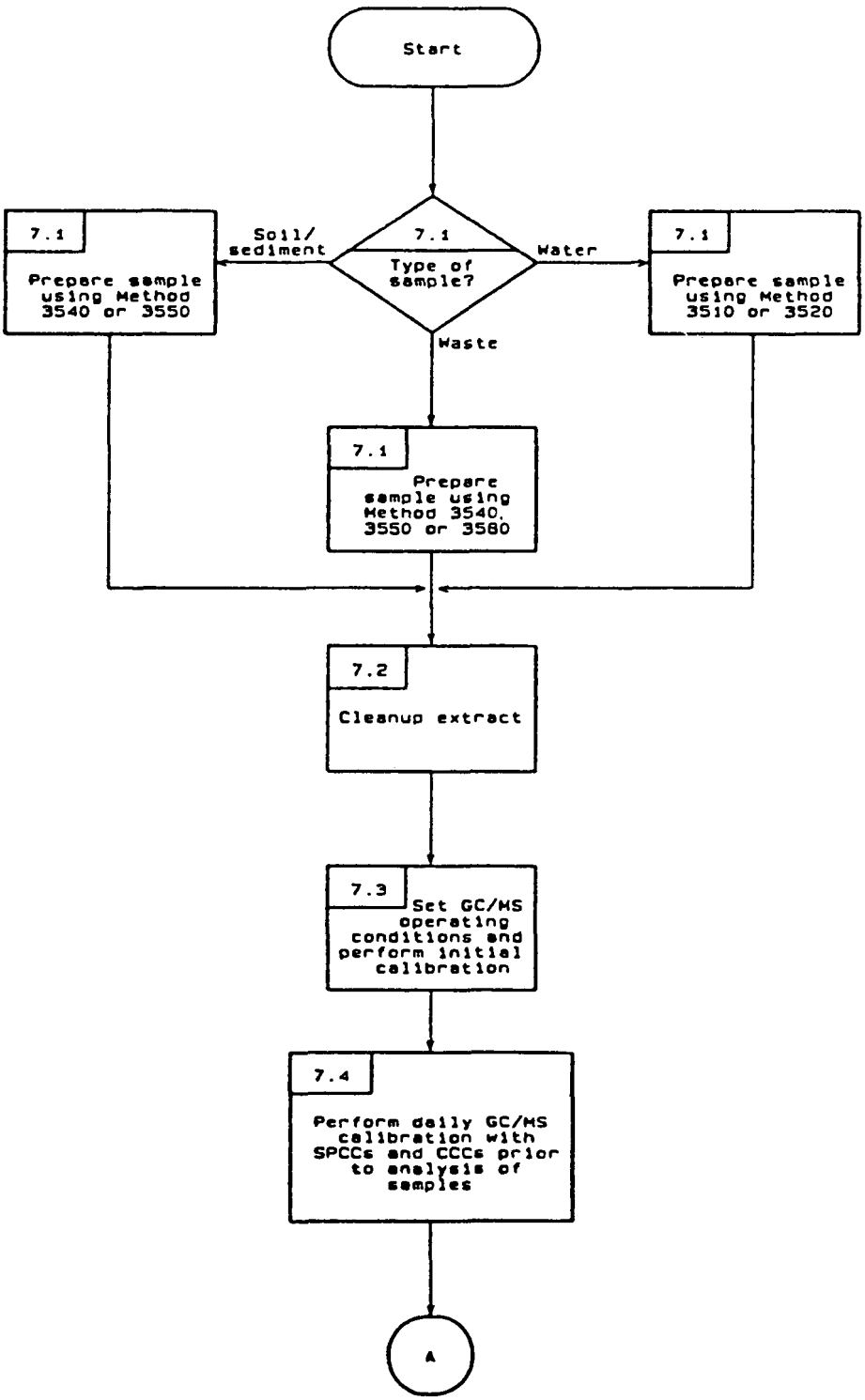
6. "Interlaboratory Method Study for EPA Method 625-Base/Neutrals, Acids, and Pesticides," Final Report for EPA Contract 68-03-3102 (in preparation).

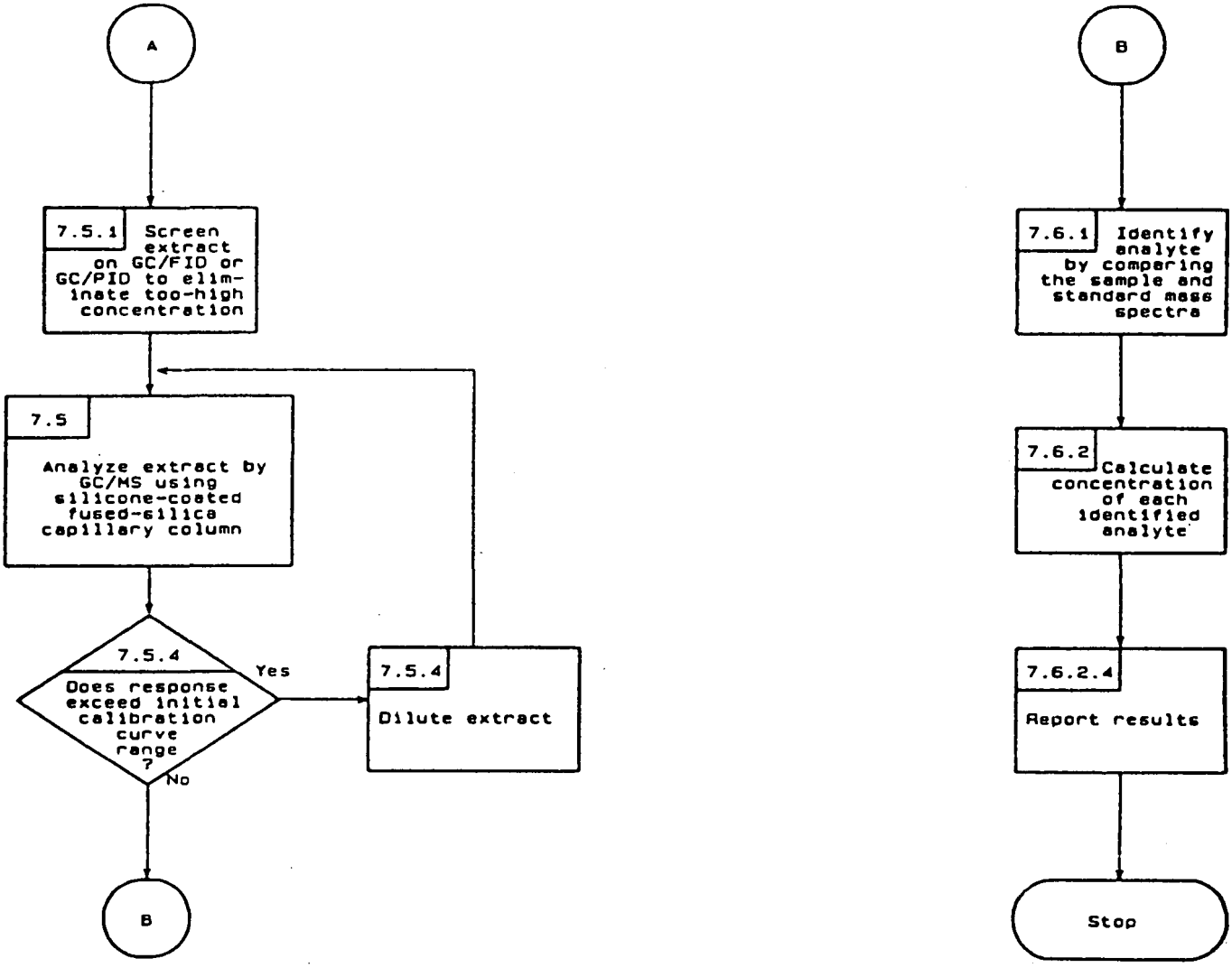
7. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

METHOD 8270

GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR SEMIVOLATILE ORGANICS:

CAPILLARY COLUMN TECHNIQUE




A
7.5.1 Screen extract on GC/FID or GC/PID to eliminate too-high concentration
7.5 Analyze extract by GC/MS using silicone-coated fused-silica capillary column
7.5.4 Does response exceed initial calibration curve range ?
Yes
No
7.5.4 Dilute extract
B
B
7.6.1 Identify analyte by comparing the sample and standard mass spectra
7.6.2 Calculate concentration of each identified analyte
7.6.2.4 Report results
Stop

METHOD 8280

THE ANALYSIS OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS

1.0 SCOPE AND APPLICATION

1.1 This method is appropriate for the determination of tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins (PCDD's) and dibenzofurans (PCDF's) in chemical wastes including still bottoms, fuel oils, sludges, fly ash, reactor residues, soil and water.

1.2 The sensitivity of this method is dependent upon the level of interferents within a given matrix. Proposed quantification levels for target analytes were 2 ppb in soil samples, up to 10 ppb in other solid wastes and 10 ppt in water. Actual values have been shown to vary by homologous series and, to a lesser degree, by individual isomer. The total detection limit for each CDD/CDF homologous series is determined by multiplying the detection limit of a given isomer within that series by the number of peaks which can be resolved under the gas chromatographic conditions.

1.3 Certain 2,3,7,8-substituted congeners are used to provide calibration and method recovery information. Proper column selection and access to reference isomer standards, may in certain cases, provide isomer specific data. Special instructions are included which measure 2,3,7,8-substituted congeners.

1.4 This method is recommended for use only by analysts experienced with residue analysis and skilled in mass spectral analytical techniques.

1.5 Because of the extreme toxicity of these compounds, the analyst must take necessary precautions to prevent exposure to himself, or to others, of materials known or believed to contain PCDD's or PCDF's. Typical infectious waste incinerators are probably not satisfactory devices for disposal of materials highly contaminated with PCDD's or PCDF's. A laboratory planning to use these compounds should prepare a disposal plan to be reviewed and approved by EPA's Dioxin Task Force (Contact Conrad Kleveno, WH-548A, U.S. EPA, 401 M Street S.W., Washington, D.C. 20450). Additional safety instructions are outlined in Appendix B.

2.0 SUMMARY OF THE METHOD

2.1 This procedure uses a matrix-specific extraction, analyte-specific cleanup, and high-resolution capillary column gas chromatography/low resolution mass spectrometry (HRGC/LRMS) techniques.

2.2 If interferents are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination. The analysis flow chart is shown in Figure 1.

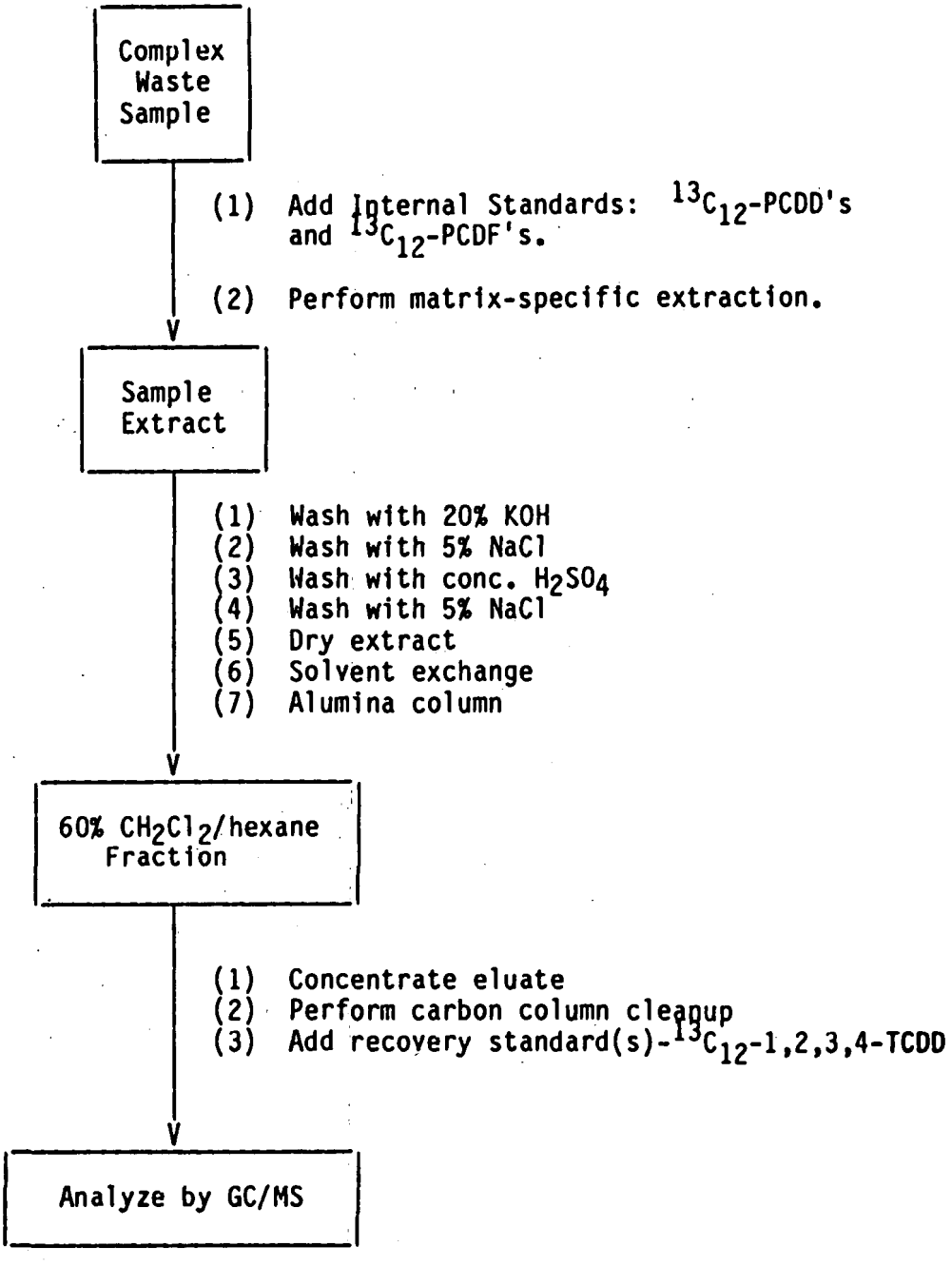


Figure 1. Method 8280 flow chart for sample extraction and cleanup as used for the analysis of PCDD's and PCDF's in complex waste samples.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines which may cause misinterpretation of chromatographic data. All of these materials must be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks.

3.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all glass systems may be required.

3.3 Interferents co-extracted from the sample will vary considerably from source to source, depending upon the industrial process being sampled. PCDD's and PCDF's are often associated with other interfering chlorinated compounds such as PCB's and polychlorinated diphenyl ethers which may be found at concentrations several orders of magnitude higher than that of the analytes of interest. Retention times of target analytes must be verified using reference standards. These values must correspond to the retention time windows established in Section 6-3. While certain cleanup techniques are provided as part of this method, unique samples may require additional cleanup techniques to achieve the method detection limit (Section 11.6) stated in Table 8.

3.4 High resolution capillary columns are used to resolve as many PCDD and PCDF isomers as possible; however, no single column is known to resolve all of the isomers.

3.5 Aqueous samples cannot be aliquoted from sample containers. The entire sample must be used and the sample container washed/rinsed out with the extracting solvent.

4.0 APPARATUS AND MATERIALS

4.1 Sampling equipment for discrete or composite sampling:

4.1.1 Grab sample bottle--amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be acid washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps--threaded to screw onto the sample bottles. Caps must be lined with Teflon. Solvent washed foil, used with the shiny side toward the sample, may be substituted for Teflon if the sample is not corrosive. Apply tape around cap to completely seal cap to bottom.

4.1.3 Compositing equipment--automatic or manual compositing system. No tygon or rubber tubing may be used, and the system must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated after sampling.

4.2 Water bath--heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

4.3 Gas chromatograph/mass spectrometer data system:

4.3.1 **Gas chromatograph:** An analytical system with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.3.2 Fused silica capillary columns are required. As shown in Table 1, three columns were evaluated using a column performance check mixture containing 1,2,3,4-TCDD, 2,3,7,8-TCDD, 1,2,3,4,7 PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, and 2,3,7,8-TCDF.

The columns include the following: (a) 50-m CP-Sil-88 programmed 60°-190° at 20°/minute, then 190°-240° at 5°/minute; (b) DB-5 (30-m x 0.25-mm I.D.; 0.25-um film thickness) programmed 170° for 10 minutes, then 170°-320° at 8°/minute, hold at 320°C for 20 minutes; (c) 30-m SP-2250 programmed 70°-320° at 10°/minute. Column/conditions (a) provide good separation of 2,3,7,8-TCDD from the other TCDD's at the expense of longer retention times for higher homologs. Column/conditions (b) and (c) can also provide acceptable separation of 2,3,7,8-TCDD. Resolution of 2,3,7,8-TCDD from the other TCDD's is better on column (c), but column (b) is more rugged, and may provide better separation from certain classes of interferents. Data presented in Figure 2 and Tables 1 to 8 of this Method were obtained using a DB-5 column with temperature programming described in (b) above. However, any capillary column which provides separation of 2,3,7,8-TCDD from all other TCDD isomers equivalent to that specified in Section 6.3 may be used; this separation must be demonstrated and documented using the performance test mixture described in Paragraph 6.3.

4.3.3 **Mass spectrometer:** A low resolution instrument is specified, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode. The system must be capable of selected ion monitoring (SIM) for at least 11 ions simultaneously, with a cycle time of 1 sec or less. Minimum integration time for SIM is 50 ms per m/z. The use of systems not capable of monitoring 11 ions simultaneously will require the analyst to make multiple injections.

4.3.4 **GC/MS interface:** Any GC-to-MS interface that gives an acceptable calibration response for each analyte of interest at the concentration required and achieves the required tuning performance criteria (see Paragraphs 6.1.-6.3) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are required. Glass can be deactivated by silanizing with dichlorodimethylsilane. Inserting a fused silica column directly into the MS source is recommended; care must be taken not to expose the end of the column to the electron beam.

4.3.5 **Data system:** A computer system must be interfaced to the mass spectrometer. The system must allow for the continuous acquisition and storage on machine-readable media of all data obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and can plot such ion abundances versus time or scan number. This type of plot

is defined as an Selected Ion Current Profile (SICP). Software must also be able to integrate the abundance, in any SICP, between specified time or scan number limits.

4.4 Pipets-Disposable, Pasteur, 150-mm long x 5-mm I.D. (Fisher Scientific Company, No. 13-678-6A, or equivalent).

4.4.1 Pipet, disposable, serological 10-mL (American Scientific Products No. P4644-10, or equivalent) for preparation of the carbon column specified in Paragraph 4.19.

4.5 Amber glass bottle (500-mL, Teflon-lined screw-cap).

4.6 Reacti-vial 2-mL, amber glass (Pierce Chemical Company). These should be silanized prior to use.

4.7 500-mL Erlenmeyer flask (American Scientific Products Cat. No. f4295 500f0) fitted with Teflon stoppers (ASP No. s9058-8, or equivalent).

4.8 Wrist Action Shaker (VWR No. 57040-049, or equivalent).

4.9 125-mL and 2-L Separatory Funnels (Fisher Scientific Company, No. 10-437-5b, or equivalent).

4.10 500-mL Kuderna-Danish fitted with a 10-mL concentrator tube and 3-ball Snyder column (Ace Glass No. 6707-02, 6707-12, 6575-02, or equivalent).

4.11 Teflon boiling chips (Berghof/American Inc., Main St., Raymond, New Hampshire 03077, No. 15021-450, or equivalent). Wash with hexane prior to use.

4.12 300-mm x 10.5-mm glass chromatographic column fitted with Teflon stopcock.

4.13 15-mL conical concentrator tubes (Kontes No. K-288250, or equivalent).

4.14 Adaptors for concentrator tubes (14/20 to 19/22) (Ace Glass No. 9092-20, or equivalent).

4.15 Nitrogen blowdown apparatus (N-Evap (reg. trademark) Analytical Evaporator Model 111, Organomation Associates Inc., Northborough, Massachusetts or equivalent). Teflon tubing connection to trap and gas regulator is required.

4.16 Microflex conical vials 2.0-mL (Kontes K-749000, or equivalent).

4.17 Filter paper (Whatman No. 54, or equivalent). Glass fiber filters or glass wool plugs are also recommended.

4.18 Solvent reservoir (125-mL) Kontes: (special order item) 12.5-cm diameter, compatible with gravity carbon column.

4.19 Carbon column (gravity flow): Prepare carbon/silica gel packing material by mixing 5 percent (by weight) active carbon AX-21 (Anderson Development Co., Adrain, Michigan), pre-washed with methanol and dried in vacuo at 110°C and 95 percent (by weight) Silica gel (Type 60, EM reagent 70 to 230 mesh, CMS No. 393-066) followed by activation of the mixture at 130° for 6 hr. Prepare a 10-mL disposable serological pipet by cutting off each end to achieve a 4-in. column. Fire polish both ends; flare if desired. Insert a glass-wool plug at one end and pack with 1 g of the carbon/silica gel mixture. Cap the packing with a glass-wool plug. (Attach reservoir to column for addition of solvents).

Option: Carbon column (HPLC): A silanized glass HPLC column (10 mm x 7 cm), or equivalent, which contains 1 g of a packing prepared by mixing 5 percent (by weight) active carbon AX-21, (Anderson Development Co., Adrian, Michigan), washed with methanol and dried in vacuo at 110°C, and 95 percent (by weight) 10 um silica (Spherisorb S10W from Phase Separations, Inc., Norwalk, Connecticut). The mixture must then be stirred and sieved through a 38-um screen (U.S. Sieve Designation 400-mesh, American Scientific Products, No. S1212-400, or equivalent) to remove any clumps.[1]

4.20 HPLC pump with loop valve (1.0 mL) injector to be used in the optional carbon column cleanup procedure.

4.21 Dean-Stark trap, 5- or 10-mL with T joints, (Fisher Scientific Company, No. 09-146-5, or equivalent) condenser and 125-mL flask.

4.22 Continuous liquid-liquid extractor (Hershberg-Wolfe type, Lab Glass No. LG-6915; or equivalent.).

4.23 Roto-evaporator, R-110. Buchi/Brinkman - American Scientific No. E5045-10; or equivalent.

5.0 REAGENTS

5.1 Potassium hydroxide (ASC): 20 percent (w/v) in distilled water.

5.2 Sulfuric acid (ACS), concentrated.

5.3 Methylene chloride, hexane, benzene, petroleum ether, methanol, tridecane, isooctane, toluene, cyclohexane. Distilled in glass or highest available purity.

5.4 Prepare stock standards in a glovebox from concentrates or neat materials. The stock solutions (50 ppm) are stored in the dark at 4°C, and checked frequently for signs of degradation or evaporation, especially just prior to the preparation of working standards.

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1 The carbon column preparation and use is adapted from W. A. Korfmacher, L. G. Rushing, D. M. Nestorick, H. C. Thompson, Jr., R. K. Mitchum, and J. R. Kominsky, Journal of High Resolution Chromatography and Chromatography Communications, 8, 12-19 (1985).

5.5 Alumina, neutral, Super 1, Woelm, 80/200 mesh. Store in a sealed container at room temperature in a desiccator over self-indicating silica gel.

5.6 Prepurified nitrogen gas.

5.7 Anhydrous sodium sulfate (reagent grade): Extracted by manual shaking with several portions of hexane and dried at 100°C.

5.8 Sodium chloride - (analytical reagent), 5 percent (w/v) in distilled water.

6.0 CALIBRATION

6.1 Two types of calibration procedures are required. One type, initial calibration, is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by results of routine calibration procedures described below. The other type, routine calibration, consists of analyzing the column performance check solution and a concentration calibration solution of 500 ng/mL (Paragraph 6.2). No samples are to be analyzed until acceptable calibration as described in Paragraphs 6.3 and 6.6 is demonstrated and documented.

6.2 Initial calibration:

6.2.1 Prepare multi-level calibration standards[2] keeping one of the recovery standards and the internal standard at fixed concentrations (500 ng/mL). Additional internal standards ($^{13}C_{12}$-OCDD 1,000 ng/mL) are recommended when quantification of the hepta- and octa-isomers is required. The use of separate internal standards for the PCDF's is also recommended. Each calibration standard should contain the following compounds:

2,3,7,8-TCDD,		
1,2,3,7,8-PeCDD	or any available	2,3,7,8,X-PeCDD isomer,
1,2,3,4,7,8-HxCDD	or any available	2,3,7,8,X,Y-HxCDD isomer,
1,2,3,4,6,7,8-HpCDD	or any available	2,3,7,8,X,Y,Z-HpCDD isomer,
2,3,7,8-TCDF		
1,2,3,7,8,PeCDF	or any available	2,3,7,8,X-PeCDF isomer,
1,2,3,4,7,8-HxCDF	or any available	2,3,7,8,X,Y,HxCDF isomer,
1,2,3,4,6,7,8-HpCDF	or any available	2,3,7,8,X,Y,Z-HpCDF isomer,

OCDD, OCDF, $^{13}C_{12}$-2,3,7,8-TCDD, $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-OCDD.

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2 $^{13}C_{12}$-labeled analytes are available from Cambridge Isotope Laboratory, Woburn, Massachusetts. Proper quantification requires the use of a specific labeled isomer for each congener to be determined. When labeled PCDD's and PCDF's of each homolog are available, their use will be required consistent with the technique of isotopic dilution.

Recommended concentration levels for standard analytes are 200, 500, 1,000, 2,000, and 5,000 ng/mL. These values may be adjusted in order to insure that the analyte concentration falls within the calibration range. Two uL injections of calibration standards should be made. However, some GC/MS instruments may require the use of a 1-uL injection volume; if this injection volume is used then all injections of standards, sample extracts and blank extracts must also be made at this injection volume. Calculation of relative response factors is described in Paragraph 11.1.2. Standards must be analyzed using the same solvent as used in the final sample extract. A wider calibration range is useful for higher level samples provided it can be described within the linear range of the method, and the identification criteria defined in Paragraph 10.4 are met. All standards must be stored in an isolated refrigerator at 4°C and protected from light. Calibration standard solutions must be replaced routinely after six months.

6.3 Establish operating parameters for the GC/MS system; the instrument should be tuned to meet the isotopic ratio criteria listed in Table 3 for PCDD's and PCDF's. Once tuning and mass calibration procedures have been completed, a column performance check mixture[3] containing the isomers listed below should be injected into the GC/MS system:

TCDD	1,3,6,8; 1,2,8,9; 2,3,7,8; 1,2,3,4; 1,2,3,7; 1,2,3,9
PeCDD	1,2,4,6,8; 1,2,3,8,9
HxCDD	1,2,3,4,6,9; 1,2,3,4,6,7
HpCDD	1,2,3,4,6,7,8; 1,2,3,4,6,7,9
OCDD	1,2,3,4,6,7,8,9
TCDF	1,3,6,8; 1,2,8,9
PeCDF	1,3,4,6,8; 1,2,3,8,9
HxCDF	1,2,3,4,6,8; 1,2,3,4,8,9
HpCDF	1,2,3,4,6,7,8; 1,2,3,4,7,8,9
OCDF	1,2,3,4,6,7,8,9

Because of the known overlap between the late-eluting tetra-isomers and the early-eluting penta-isomers under certain column conditions, it may be necessary to perform two injections to define the TCDD/TCDF and PeCDD/PeCDF elution windows, respectively. Use of this performance check mixture will enable the following parameters to be checked: (a) the retention windows for each of the homologues, (b) the GC resolution of 2,3,7,8-TCDD and 1,2,3,4-TCDD, and (c) the relative ion abundance criteria listed for PCDD's and PCDF's in Table 3. GC column performance should be checked daily for resolution and peak shape using this check mixture.

The chromatographic peak separation between 2,3,7,8-TCDD and 1,2,3,4-TCDD must be resolved with a valley of $\leq$25 percent, where

$$\text{Valley Percent} = (x/y)\ (100)$$

x = measured as in Figure 2
y = the peak height of 2,3,7,8-TCDD

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3 Performance check mixtures are available from Brehm Laboratory, Wright State University, Dayton, Ohio.

It is the responsibility of the laboratory to verify the conditions suitable for maximum resolution of 2,3,7,8-TCDD from all other TCDD isomers. The peak representing 2,3,7,8-TCDD should be labeled and identified as such on all chromatograms.

6.4 Acceptable SIM sensitivity is verified by achieving a minimum signal-to-noise ratio of 50:1 for the m/z 320 ion of 2,3,7,8-TCDD obtained from injection of the 200 ng/mL calibration standard.

6.5 From injections of the 5 calibration standards, calculate the relative response factors (RRF's) of analytes vs. the appropriate internal standards, as described in Paragraph 11.1.2. Relative response factors for the hepta- and octa-chlorinated CDD's and CDF's are to be calculated using the corresponding $^{13}C_{12}$-octachlorinated standards.

6.6 For each analyte calculate the mean relative response factor (RRF), the standard deviation, and the percent relative standard deviation from triplicate determinations of relative response factors for each calibration standard solution.

6.7 The percent relative standard deviations (based on triplicate analysis) of the relative response factors for each calibration standard solution should not exceed 15 percent. If this condition is not satisfied, remedial action should be taken.

6.8 The Laboratory must not proceed with analysis of samples before determining and documenting acceptable calibration with the criteria specified in Paragraphs 6.3 and 6.7.

6.9 Routine calibration:

6.9.1 Inject a 2-uL aliquot of the column performance check mixture. Acquire at least five data points for each GC peak and use the same data acquisition time for each of the ions being monitored.

NOTE: The same data acquisition parameters previously used to analyze concentration calibration solutions during initial calibration must be used for the performance check solution. The column performance check solution must be run at the beginning and end of a 12 hr period. If the contractor laboratory operates during consecutive 12-hr periods (shifts), analysis of the performance check solution at the beginning of each 12-hr period and at the end of the final 12-hr period is sufficient.

Determine and document acceptable column performance as described in Paragraph 6.3.

6.9.2 Inject a 2-uL aliquot of the calibration standard solution at 500 ng/mL at the beginning of a 2-hr period. Determine and document acceptable calibration as specified in Paragraph 6.3, i.e., SIM sensitivity and relative ion abundance criteria. The measured RRF's of

all analytes must be within +30 percent of the mean values established by initial analyses of the calibration standard solutions.

7.0 QUALITY CONTROL

7.1 Before processing any samples, the analyst must demonstrate through the analysis of a method blank that all glassware and reagents are interferent-free at the method detection limit of the matrix of interest. Each time a set of samples is extracted, or there is a change in reagents, a method blank must be processed as a safeguard against laboratory contamination.

7.2 A laboratory "method blank" must be run along with each analytical batch (20 or fewer samples). A method blank is performed by executing all of the specified extraction and cleanup steps, except for the introduction of a sample. The method blank is also dosed with the internal standards. For water samples, one liter of deionized and/or distilled water should be used as the method blank. Mineral oil may be used as the method blank for other matrices.

7.3 The laboratory will be expected to analyze performance evaluation samples as provided by the EPA on a periodic basis throughout the course of a given project. Additional sample analyses will not be permitted if the performance criteria are not achieved. Corrective action must be taken and acceptable performance must be demonstrated before sample analyses can resume.

7.4 Samples may be split with other participating labs on a periodic basis to ensure interlaboratory consistency. At least one sample per set of 24 must be run in duplicate to determine intralaboratory precision.

7.5 Field duplicates (individual samples taken from the same location at the same time) should be analyzed periodically to determine the total precision (field and lab).

7.6 Where appropriate, "field blanks" will be provided to monitor for possible cross-contamination of samples in the field. The typical "field blank" will consist of uncontaminated soil (background soil taken off-site).

7.7 GC column performance must be demonstrated initially and verified prior to analyzing any sample in a 12-hr period. The GC column performance check solution must be analyzed under the same chromatographic and mass spectrometric conditions used for other samples and standards.

7.8 Before using any cleanup procedure, the analyst must process a series of calibration standards (Paragraph 6.2) through the procedure to validate elution patterns and the absence of interferents from reagents. Both alumina column and carbon column performance must be checked. Routinely check the 8 percent CH_2Cl_2/hexane eluate of environmental extracts from the alumina column for presence of target analytes.

NOTE: This fraction is intended to contain a high level of interferents and analysis near the method detection limit may not be possible.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Grab and composite samples must be collected in glass containers. Conventional sampling practices must be followed. The bottle must not be prewashed with sample before collection. Composite samples should be collected in glass containers. Sampling equipment must be free of tygon, rubber tubing, other potential sources of contamination which may absorb the target analytes.

8.2 All samples must be stored at 4°C, extracted within 30 days and completely analyzed within 45 days of collection.

9.0 EXTRACTION AND CLEANUP PROCEDURES

9.1 Internal standard addition. Use a sample aliquot of 1 g to 1,000 mL (typical sample size requirements for each type of matrix are provided in Paragraph 9.2) of the chemical waste or soil to be analyzed. Transfer the sample to a tared flask and determine the weight of the sample. Add an appropriate quantity of $^{13}C_{12}$-2,3,7,8-TCDD, and any other material which is to be used as an internal standard, (Paragraph 6.2). All samples should be spiked with at least one internal standard, for example, $^{13}C_{12}$-2,3,7,8-TCDD, to give a concentration of 500 ng/mL in the final concentrated extract. As an example, a 10 g sample concentrated to a final volume of 100 uL requires the addition of 50 ng of $^{13}C_{12}$-2,3,7,8-TCDD, assuming 100% recovery. Adoption of different calibration solution sets (as needed to achieve different quantification limits for different congeners) will require a change in the fortification level. Individual concentration levels for each homologous series must be specified.

9.2 Extraction

9.2.1 **Sludge/fuel oil.** Extract aqueous sludge samples by refluxing a sample (e.g. 2 g) with 50 mL of toluene (benzene) in a 125-mL flask fitted with a Dean-Stark water separator. Continue refluxing the sample until all the water has been removed. Cool the sample, filter the toluene extract through a fiber filter, or equivalent, into a 100-mL round bottom flask. Rinse the filter with 10 mL of toluene, combine the extract and rinsate. Concentrate the combined solution to near dryness using a rotary evaporator at 50°C. Use of an inert gas to concentrate the extract is also permitted. Proceed with Step 9.2.4.

9.2.2 **Still bottom.** Extract still bottom samples by mixing a sample (e.g., 1.0 g) with 10 mL of toluene (benzene) in a small beaker and filtering the solution through a glass fiber filter (or equivalent) into a 50-mL round bottom flask. Rinse the beaker and filter with 10 mL of toluene. Concentrate the combined toluene solution to near dryness using a rotary evaporator at 50°C while connected to a water aspirator. Proceed with Step 9.2.4.

9.2.3 **Fly ash.** Extract fly ash samples by placing a sample (e.g. 10 g) and an equivalent amount of anhydrous sodium sulfate in a Soxhlet extraction apparatus charged with 100 mL of toluene (benzene) and extract for 16 hr using a three cycle/hour schedule. Cool and filter the toluene extract through a glass fiber filter paper into a 500-mL round bottom flask. Rinse the filter with 5 mL of toluene. Concentrate the combined toluene solution to near dryness using a rotary evaporator at 50°C. Proceed with Step 9.2.4.

9.2.4 Transfer the residue to a 125-mL separatory funnel using 15 mL of hexane. Rinse the flask with two 5-mL aliquots of hexane and add the rinses to the funnel. Shake 2 min with 50 mL of 5% NaCl solution, discard the aqueous layer and proceed with Step 9.3.

9.2.5 **Soil.** Extract soil samples by placing the sample (e.g. 10 g) and an equivalent amount of anhydrous sodium sulfate in a 500-mL Erlenmeyer flask fitted with a Teflon stopper. Add 20 mL of methanol and 80 mL of petroleum ether, in that order, to the flask. Shake on a wrist-action shaker for two hr. The solid portion of sample should mix freely. If a smaller soil aliquot is used, scale down the amount of methanol proportionally.

9.2.5.1 Filter the extract from Paragraph 9.2.5 through a glass funnel fitted with a glass fiber filter and filled with anhydrous sodium sulfate into a 500-mL Kuderna-Danish (KD) concentrator fitted with a 10-mL concentrator tube. Add 50 mL of petroleum ether to the Erlenmeyer flask, restopper the flask and swirl the sample gently, remove the stopper carefully and decant the solvent through the funnel as above. Repeat this procedure with two additional 50-mL aliquots of petroleum ether. Wash the sodium sulfate in the funnel with two additional 5-mL portions of petroleum ether.

9.2.5.2 Add a Teflon or PFTE boiling chip and a three-ball Snyder column to the KD flask. Concentrate in a 70°C water bath to an apparent volume of 10 mL. Remove the apparatus from the water bath and allow it to cool for 5 min.

9.2.5.3 Add 50 mL of hexane and a new boiling chip to the KD flask. Concentrate in a water bath to an apparent volume of 10 mL. Remove the apparatus from the water bath and allow to cool for 5 min.

9.2.5.4 Remove and invert the Snyder column and rinse it down into the KD with two 1-mL portions of hexane. Decant the contents of the KD and concentrator tube into a 125-mL separatory funnel. Rinse the KD with two additional 5-mL portions of hexane, combine. Proceed with Step 9.3.

9.2.6 **Aqueous samples:** Mark the water meniscus on the side of the 1-L sample bottle for later determination of the exact sample volume.

Pour the entire sample (approximately 1-L) into a 2-L separatory funnel. Proceed with Step 9.2.6.1.

NOTE: A continuous liquid-liquid extractor may be used in place of a separatory funnel when experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered using a separatory funnel. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 sec to rinse the inner surface. Transfer the solvent to the extractor. Repeat the sample bottle rinse with an additional 50- to 100-mL portion of methylene chloride and add the rinse to the extractor. Add 200 to 500 mL of methylene chloride to the distilling flask; add sufficient reagent water to ensure proper operation, and extract for 24 hr. Allow to cool, then detach the distilling flask. Dry and concentrate the extract as described in Paragraphs 9.2.6.1 and 9.2.6.2. Proceed with Paragraph 9.2.6.3.

9.2.6.1 Add 60 mL methylene chloride to the sample bottle, seal and shake 30 sec to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. Collect the methylene chloride (3 x 60 mL) directly into a 500-mL Kuderna-Danish concentrator (mounted with a 10-mL concentrator tube) by passing the sample extracts through a filter funnel packed with a glass wool plug and 5 g of anhydrous sodium sulfate. After the third extraction, rinse the sodium sulfate with an additional 30 mL of methylene chloride to ensure quantitative transfer.

9.2.6.2 Attach a Snyder column and concentrate the extract on a water bath until the apparent volume of the liquid reaches 5 mL. Remove the K-D apparatus and allow it to drain and cool for at least 10 min. Remove the Snyder column, add 50 mL hexane, re-attach the Snyder column and concentrate to approximately 5 mL. Add a new boiling chip to the K-D apparatus before proceeding with the second concentration step.

Rinse the flask and the lower joint with 2 x 5 mL hexane and combine rinses with extract to give a final volume of about 15 mL.

9.2.6.3 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1,000-mL graduated cylinder. Record the sample volume to the nearest 5 mL. Proceed with Paragraph 9.3.

9.3 In a 250-mL Separatory funnel, partition the solvent (15 mL hexane) against 40 mL of 20 percent (w/v) potassium hydroxide. Shake for 2 min.

Remove and discard the aqueous layer (bottom). Repeat the base washing until no color is visible in the bottom layer (perform base washings a maximum of four times). Strong base (KOH) is known to degrade certain PCDD/PCDF's, contact time must be minimized.

9.4 Partition the solvent (15 mL hexane) against 40 mL of 5 percent (w/v) sodium chloride. Shake for 2 min. Remove and discard aqueous layer (bottom).

NOTE: Care should be taken due to the heat of neutralization and hydration.

9.5 Partition the solvent (15 mL hexane) against 40 mL of concentrated sulfuric acid. Shake for 2 min. Remove and discard the aqueous layer (bottom). Repeat the acid washings until no color is visible in the acid layer. (Perform acid washings a maximum of four times.)

9.6 Partition the extract against 40 mL of 5 percent (w/v) sodium chloride. Shake for 2 min. Remove and discard the aqueous layer (bottom). Dry the organic layer by pouring through a funnel containing anhydrous sodium sulfate into a 50-mL round bottom flask, wash the separatory funnel with two 15-mL portions of hexane, pour through the funnel, and combine the hexane extracts. Concentrate the hexane solution to near dryness with a rotary evaporator (35°C water bath), making sure all traces of toluene are removed. (Use of blowdown with an inert gas to concentrate the extract is also permitted).

9.7 Pack a gravity column (glass 300-mm x 10.5-mm), fitted with a Teflon stopcock, in the following manner:

Insert a glass-wool plug into the bottom of the column. Add a 4-g layer of sodium sulfate. Add a 4-g layer of Woelm super 1 neutral alumina. Tap the top of the column gently. Woelm super 1 neutral alumina need not be activated or cleaned prior to use but should be stored in a sealed desiccator. Add a 4-g layer of sodium sulfate to cover the alumina. Elute with 10 mL of hexane and close the stopcock just prior to the exposure of the sodium sulfate layer to air. Discard the eluant. Check the column for channeling. If channeling is present discard the column. Do not tap a wetted column.

9.8 Dissolve the residue from Step 9.6 in 2 mL of hexane and apply the hexane solution to the top of the column. Elute with enough hexane (3-4 mL) to complete the transfer of the sample cleanly to the surface of the alumina. Discard the eluant.

9.8.1 Elute with 10 mL of 8 percent (v/v) methylene chloride in hexane. Check by GC/MS analysis that no PCDD's or PCDF's are eluted in this fraction. See Paragraph 9.9.1.

9.8.2 Elute the PCDD's and PCDF's from the column with 15 mL of 60 percent (v/v) methylene chloride in hexane and collect this fraction in a conical shaped (15-mL) concentrator tube.

9.9 Carbon column cleanup:

Prepare a carbon column as described in Paragraph 4.18.

9.9.1 Using a carefully regulated stream of nitrogen (Paragraph 4.15), concentrate the 8 percent fraction from the alumina column (Paragraph 9.8.1) to about 1 mL. Wash the sides of the tube with a small volume of hexane (1 to 2 mL) and reconcentrate to about 1 mL. Save this 8 percent concentrate for GC/MS analysis to check for breakthrough of PCDD's and PCDF's. Concentrate the 60 percent fraction (Paragraph 9.8.2) to about 2 to 3 mL. Rinse the carbon with 5 mL cyclohexane/methylene chloride (50:50 v/v) in the forward direction of flow and then in the reverse direction of flow. While still in the reverse direction of flow, transfer the sample concentrate to the column and elute with 10 mL of cyclohexane/methylene chloride (50:50 v/v) and 5 mL of methylene chloride/methanol/benzene (75:20:5, v/v). Save all above eluates and combine (this fraction may be used as a check on column efficiency). Now turn the column over and in the direction of forward flow elute the PCDD/PCDF fraction with 20 mL toluene.

NOTE: Be sure no carbon fines are present in the eluant.

9.9.2 Alternate carbon column cleanup. Proceed as in Section 9.9.1 to obtain the 60 percent fraction re-concentrated to 400 uL which is transferred to an HPLC injector loop (1 mL). The injector loop is connected to the optional column described in Paragraph 4.18. Rinse the centrifuge tube with 500 uL of hexane and add this rinsate to the injector loop. Load the combined concentrate and rinsate onto the column. Elute the column at 2 mL/min, ambient temperature, with 30 mL of cyclohexane/methylene chloride 1:1 (v/v). Discard the eluant. Backflush the column with 40 mL toluene to elute and collect PCDD's and PCDF's (entire fraction). The column is then discarded and 30 mL of cyclohexane/methylene chloride 1:1 (v/v) is pumped through a new column to prepare it for the next sample.

9.9.3 Evaporate the toluene fraction to about 1 mL on a rotary evaporator using a water bath at 50°C. Transfer to a 2.0-mL Reacti-vial using a toluene rinse and concentrate to the desired volume using a stream of N_2. The final volume should be 100 uL for soil samples and 500 uL for sludge, still bottom, and fly ash samples; this is provided for guidance, the correct volume will depend on the relative concentration of target analytes. Extracts which are determined to be outside the calibration range for individual analytes must be diluted or a smaller portion of the sample must be re-extracted. Gently swirl the solvent on the lower portion of the vessel to ensure complete dissolution of the PCDD's and PCDF's.

9.10 Approximately 1 hr before HRGC/LRMS analysis, transfer an aliquot of the extract to a micro-vial (Paragraph 4.16). Add to this sufficient recovery standard ($^{13}C_{12}$1,2,3,4-TCDD) to give a concentration of 500 ng/mL. (Example: 36 uL aliquot of extract and 4 uL of recovery standard solution. Remember to adjust the final result to correct for this dilution. Inject an appropriate aliquot (1 or 2 uL) of the sample into the GC/MS instrument.

10.0 GC/MS ANALYSIS

10.1 When toluene is employed as the final solvent use of a bonded phase column from Paragraph 4.3.2 is recommended. Solvent exchange into tridecane is required for other liquid phases or nonbonded columns (CP-Sil-88).

NOTE: Chromatographic conditions must be adjusted to account for solvent boiling points.

10.2 Calculate response factors for standards relative to the internal standards, $^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-OCDD (see Section 11). Add the recovery standard ($^{13}C_{12}$-1,2,3,4-TCDD) to the samples prior to injection. The concentration of the recovery standard in the sample extract must be the same as that in the calibration standards used to measure the response factors.

10.3 Analyze samples with selected ion monitoring, using all of the ions listed in Table 2. It is recommended that the GC/MS run be divided into five selected ion monitoring sections, namely: (1) 243, 257,, 304, 306, 320, 322, 332, 334, 340, 356, 376 (TCDD's, TCDF's, $^{13}C_{12}$-labeled internal and recovery standards, PeCDD's, PeCDF's, HxCDE); (2) 277, 293, 306, 332, 338, 340, 342, 354, 356, 358, 410 (peCDD's, PeCDF's, HpCDE); (3) 311, 327, 340, 356, 372, 374, 376, 388, 390, 392, 446, (HxCDD's, HxCDF's, OCDE); (4) 345, 361, 374, 390, 406, 408, 410, 422, 424, 426, 480 (HpCDD's, HpCDF's, NCDE) and (5) 379, 395, 408, 424, 442, 444, 458, 460, 470, 472, 514 (OCDD, OCDF, $^{13}C_{12}$-OCDD, DCDE). Cycle time not to exceed 1 sec/descriptor. It is recommended that selected ion monitoring section 1 should be applied during the GC run to encompass the retention window (determined in Paragraph 6.3) of the first- and last-eluting tetra-chlorinated isomers. If a response is observed at m/z 340 or 356, then the GC/MS analysis must be repeated; selected ion monitoring section 2 should then be applied to encompass the retention window of the first- and last-eluting penta-chlorinated isomers. HxCDE, HpCDE, OCDE, NCDE, DCDE, are abbreviations for hexa-, hepta-, octa-, nona-, and decachlorinated diphenyl ether, respectively.

10.4 Identification criteria for PCDD's and PCDF's:

10.4.1 All of the characteristic ions, i.e. quantitation ion, confirmation ions, listed in Table 2 for each class of PCDD and PCDF, must be present in the reconstructed ion chromatogram. It is desirable that the M - COCl ion be monitored as an additional requirement. Detection limits will be based on quantitation ions within the molecules in cluster.

10.4.2 The maximum intensity of each of the specified characteristic ions must coincide within 2 scans or 2 sec.

10.4.3 The relative intensity of the selected, isotopic ions within the molecular ion cluster of a homologous series of PCDD's of PCDF's must lie within the range specified in Table 3.

10.4.4 The GC peaks assigned to a given homologous series must have retention times within the window established for that series by the column performance solution.

10.5 Quantitate the PCDD and PCDF peaks from the response relative to the appropriate internal standard. Recovery of each internal standard) vs. the recovery standard must be greater than 40 percent. It is recommended that samples with recoveries of less than 40 percent or greater than 120 percent be re-extracted and re-analyzed.

NOTE: These criteria are used to assess method performance; when properly applied, isotope dilution techniques are independent of internal standard recovery.

In those circumstances where these procedures do not yield a definitive conclusion, the use of high resolution mass spectrometry or HRGC/MS/MS is suggested.

11.0 CALCULATIONS

NOTE: The relative response factors of a given congener within any homologous series are known to be different. However, for purposes of these calculations, it will be assumed that every congener within a given series has the same relative response factor. In order to minimize the effect of this assumption on risk assessment, a 2,3,7,8-substituted isomer that is commercially available was chosen as representative of each series. All relative response factor calculations for a given homologous series are based on that compound.

11.1 Determine the concentration of individual isomers of tetra-, penta, and hexa-CDD/CDF according to the equation:

$$\text{Concentration, ng/g} = \frac{Q_{is} \times A_s}{G \times A_{is} \times RRF}$$

where:

Q_{is} = ng of internal standard $^{13}C_{12}$-2,3,7,8-TCDD, added to the sample before extraction.

G = g of sample extracted.

A_s = area of quantitation ion of the compound of interest.

A_{is} = area of quantitation ion (m/z 334) of the internal standard, $^{13}C_{12}$-2,3,7,8-TCDD.

RRF = response factor of the quantitation ion of the compound of interest relative to m/z 334 of $^{13}C_{12}$-2,3,7,8-TCDD.

NOTE: Any dilution factor introduced by following the procedure in Paragraph 9.10 should be applied to this calculation.

11.1.1 Determine the concentration of individual isomers of hepta-CDD/CDF and the concentration of OCDD and OCDF according to the equation:

$$\text{Concentration, ng/g} = \frac{Q_{is} \times A_s}{G \times A_{is} \times RRF}$$

where:

Q_{is} = ng of internal standard $^{13}C_{12}$-OCDD, added to the sample before extraction.

G = g of sample extracted.

A_s = area of quantitation ion of the compound of interest.

A_{is} = area of quantitation ion (m/z 472) of the internal standard, $^{13}C_{12}$-OCDD.

RRF = response factor of the quantitation ion of the compound of interest relative to m/z 472 of $^{13}C_{12}$-OCDD.

NOTE: Any dilution factor introduced by following the procedure in Paragraph 9.10 should be applied to this calculation.

11.1.2 Relative response factors are calculated using data obtained from the analysis of multi-level calibration standards according to the equation:

$$RRF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = area of quantitation ion of the compound of interest.

A_{is} = area of quantitation ion of the appropriate internal standard (m/z 334 for $^{13}C_{12}$-2,3,7,8-TCDD; m/z 472 for $^{13}C_{12}$-OCDD).

C_{is} = concentration of the appropriate internal standard, $^{13}C_{12}$-2,3,7,8-TCDD or $^{13}C_{12}$-OCDD)

C_s = concentration of the compound of interest.

11.1.3 The concentrations of unknown isomers of TCDD shall be calculated using the mean RRF determined for 2,3,7,8-TCDD.

The concentrations of unknown isomers of PeCDD shall be calculated using the mean RRF determined for 1,2,3,7,8-PeCDD or any available 2,3,7,8,X-PeCDD isomer.

The concentrations of unknown isomers of HxCDD shall be calculated using the mean RRF determined for 1,2,3,4,7,8-HxCDD or any available 2,3,7,8,-X,Y-HXCDD isomer.

The concentrations of unknown isomers of HpCDD shall be calculated using the mean RRF determined for 1,2,3,4,6,7,8-HpCDD or any available 2,3,7,8,X,Y,Z-HpCDD isomer.

The concentrations of unknown isomers of TCDF shall be calculated using the mean RRF determined for 2,3,7,8-TCDF.

The concentrations of unknown isomers of PeCDF shall be calculated using the mean RRF determined for 1,2,3,7,8-PeCDF or any available 2,3,7,8,X-PeCDF isomer.

The concentrations of unknown isomers of HxCDF shall be calculated using the mean RRF determined for 1,2,4,7,8-HxCDF or any available 2,3,7,8-X,Y-HxCDF isomer.

The concentrations of unknown isomers of HpCDF shall be calculated using the mean RRF determined for 1,2,3,4,6,7,8-HpCDF or any available 2,3,7,8,X,Y,Z-HpCDF isomer.

The concentration of the octa-CDD and octa-CDF shall be calculated using the mean RRF determined for each.

Mean relative response factors for selected PCDD's and PCDF's are given in Table 4.

11.1.4 Calculate the percent recovery, R_{is}, for each internal standard in the sample extract, using the equation:

$$R_{is} = \frac{A_{is} \times Q_{rs}}{A_{rs} \times RF_r \times Q_{is}} = 100\%$$

where:

A_{rs} = Area of quantitation ion (m/z 334) of the recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD.

Q_{rs} = ng of recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD, added to extract.

The response factor for determination of recovery is calculated using data obtained from the analysis of the multi-level calibration standards according to the equation:

$$RF_r = \frac{A_{is} \times C_{rs}}{A_{rs} \times C_{is}}$$

where:

C_{rs} = Concentration of the recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD.

11.1.5 Calculation of total concentration of all isomers within each homologous series of PCDD's and PCDF's.

Total concentration of PCDD's or PCDF's = Sum of the concentrations of the individual PCDD or PCDF isomers

11.4 Report results in nanograms per gram; when duplicate and spiked samples are reanalyzed, all data obtained should be reported.

11.5 Accuracy and Precision. Table 5 gives the precision data for revised Method 8280 for selected analytes in the matrices shown. Table 6 lists recovery data for the same analyses. Table 2 shows the linear range and variation of response factors for selected analyte standards. Table 8 provides the method detection limits as measured in specific sample matrices.

11.6 Method Detection Limit. The Method Detection Limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the value is above zero. The procedure used to determine the MDL values reported in Table 8 was obtained from Appendix A of EPA Test Methods manual, EPA-600/4-82-057 July 1982, "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater."

11.7 Maximum Holding Time (MHT). Is that time at which a 10 percent change in the analyte concentration (C_{t10}) occurs and the precision of the method of measurement allows the 10 percent change to be statistically different from the 0 percent change (C_{t0}) at the 90 percent confidence level. When the precision of the method is not sufficient to statistically discriminate a 10 percent change in the concentration from 0 percent change, then the maximum holding time is that time where the percent change in the analyte concentration (C_{tn}) is statistically different than the concentration at 0 percent change (C_{t0}) and greater than 10 percent change at the 90 percent confidence level.

TABLE 1. REPRESENTATIVE GAS CHROMATOGRAPH RETENTION TIMES* OF ANALYTES

Analyte	50-m CP-Sil-88	30-m DB-5	3--m SP-2250
2,3,7,8-TCDF	25.2	17.8	26.7
2,3,7,8-TCDD	23.6	17.4	26.7
1,2,3,4-TCDD	24.1	17.3	26.5
1,2,3,4,7-PeCDD	30.0	20.1	28.1
1,2,3,4,7,8-HxCDD	39.5	22.1	30.6
1,2,3,4,6,7,8-HpCDD	57.0	24.1	33.7
OCDD	NM	25.6	NM

*Retention time in min, using temperature programs shown below.

NM = not measured.

Temperature Programs:

CP-Sil-88	60°C-190°C at 20°/min; 190°-240° at 5°/min.
DB-5 30 m x 0.25 mm Thin film (0.25 um)	170°, 10 min; then at 8°/min to 320°C, hold at 320°C 20 min (until OCDD elutes).
SP-2250	70°-320° at 10°/minute.

Column Manufacturers

CP-Sil-88	Chrompack, Incorporated, Bridgewater, New Jersey
DB-5,	J and W Scientific, Incorporated, Rancho Cordova, California
SP-2250	Supelco, Incorporated, Bellefonte, Pennsylvania

TABLE 2. IONS SPECIFIED[a] FOR SELECTED ION MONITORING FOR PCDD'S AND PCDF'S

	Quantitation ion	Confirmation ions	M-COCl
PCDD's			
$^{13}C_{12}$-Tetra	334	332	---
Tetra	322	320	257
Penta	356	354;358	293
Hexa	390	388;392	327
Hepta	424	422;426	361
Octa	460	458	395
$^{13}C_{12}$-Octa	472	470	
PCDF's			
Tetra	306	304	243
Penta	340	338;342	277
Hexa	374	372;376	311
Hepta	408	406;410	345
Octa	444	442	379

[a]Ions at m/z 376 (HxCDE), 410 (HpCDE), 446 (OCDE), 480 (NCDE) and 514 (DCDE) are also included in the scan monitoring sections (1) to (5), respectively. See Paragraph 10.3.

TABLE 3. CRITERIA FOR ISOTOPIC RATIO MEASUREMENTS FOR PCDD'S AND PCDF'S

	Selected ions (m/z)	Relative intensity
PCDD's		
Tetra	320/322	0.65-0.89
Penta	358/356	0.55-0.75
Hexa	392/390	0.69-0.93
Hepta	426/424	0.83-1.12
Octa	458/460	0.75-1.01
PCDF's		
Tetra	304/306	0.65-0.89
Penta	342/340	0.55-0.75
Hexa	376/374	0.69-0.93
Hepta	410/408	0.83-1.12
Octa	442/444	0.75-1.01

TABLE 4. MEAN RELATIVE RESPONSE FACTORS OF CALIBRATION STANDARDS

Analyte	RRF[a]	RSD% (n = 5)	Quantitation ion (m/z)
2,3,7,8-TCDD	1.13	3.9	322
1,2,3,7,8-PeCDD	0.70	10.1	356
1,2,3,4,7,8-HxCDD	0.51	6.6	390
1,2,3,4,6,7,8-HpCDD[b]	1.08	6.6	424
OCDD[b]	1.30	7.2	460
2,3,7,8-TCDF	1.70	8.0	306
1,2,3,7,8-PeCDF	1.25	8.7	340
1,2,3,4,7,8-HxCDF	0.84	9.4	374
1,2,3,4,6,7,8-HpCDF[b]	1.19	3.8	444
OCDF[b]	1.57	8.6	408
$^{13}C_{12}$-2,3,7,8-TCDD	1.00	-	334
$^{13}C_{12}$-1,2,3,4-TCDD	0.75	4.6	334
$^{13}C_{12}$-OCDD	1.00	-	472

[a]The RRF value is the mean of the five determinations made. Nominal weights injected were 0.2, 0.5, 1.0, 2.0 and 5.0 ng.

[b]RRF values for these analytes were determined relative to $^{13}C_{12}$-OCDD. All other RRF's were determined relative to $^{13}C_{12}$-2,3,7,8-TCDD.

Instrument Conditions/Tune - GC/MS system was tuned as specified in Paragraph 6.3. RRF data was acquired under SIM control, as specified in Paragraph 10.3.

GC Program - The GC column temperature was programmed as specified in Paragraph 4.3.2(b).

TABLE 5. PRECISION DATA FOR REVISED METHOD 8280

Compound	Matrix[a]	Analyte level (ng/g) Native	Native + spike	N	Percent RSD
2,3,7,8-TCDD	clay	ND[b]	5.0	4	4.4
	soil	378	378	4	2.8
	sludge	ND	125	4	4.8
	fly ash	ND	46	2	-
	still bottom	487	487	4	24
1,2,3,4-TCDD	clay	ND	5.0	3	1.7
	soil	ND	25.0	4	1.1
	sludge	ND	125	4	9.0
	fly ash	38.5	38.5	4	7.9
	still bottom	ND	2500	4	-
1,3,6,8-TCDD	clay	ND	2.5	4	7.0
	soil	ND	25.0	4	5.1
	sludge	ND	125	4	3.1
	fly ash	19.1	19.1	2	-
	still bottom	227	2727	2	-
1,3,7,9-TCDD	clay	ND	2.5	4	19
	soil	ND	25.0	4	2.3
	sludge	ND	125.0	4	6.5
	fly ash	58.4	58.4	2	-
	still bottom	ND	2500	2	-
1,3,7,8-TCDD	clay	ND	5.0	4	7.3
	soil	ND	25.0	4	1.3
	sludge	ND	125	4	5.8
	fly ash	16.0	16.0	4	3.5
	still bottom	422	2920	2	-
1,2,7,8-TCDD	clay	ND	5.0	4	7.7
	soil	ND	25.0	4	9.0
	sludge	ND	125	4	7.7
	fly ash	2.6	2.6	3	23
	still bottom	ND	2500	2	-
1,2,8,9-TCDD	clay	ND	5.0	4	10
	soil	ND	25.0	4	0.6
	sludge	ND	125	4	1.9
	fly ash	ND	46	2	-
	still bottom	ND	2500	2	-

TABLE 5 (Continued)

Compound	Matrix[a]	Analyte level (ng/g) Native	Native + spike	N	Percent RSD
1,2,3,4,7-PeCDD	clay	ND	5.0	4	10
	soil	ND	25.0	4	2.8
	sludge	ND	125	4	4.6
	fly ash	25.8	25.8	2	6.9
	still bottom	ND	2500	2	-
1,2,3,7,8-PeCDD	clay	ND	5.0	4	25
	soil	ND	25.0	4	20
	sludge	ND	125	4	4.7
	fly ash	ND	46	2	-
	still bottom	ND	2500	2	-
1,2,3,4,7,8-HxCDD	clay	ND	5.0	4	38
	soil	ND	25.0	4	8.8
	sludge	ND	125	4	3.4
	fly ash	ND	46	2	-
	still bottom	ND	2500	2	-
1,2,3,4,6,7,8-HpCDD	clay	ND	5.0	4	-
	soil	ND	25.0	4	-
	sludge[c]	8760	8780	4	-
	fly ash	ND	-	-	-
	still bottom	ND	-	-	-
1,2,7,8-TCDF	clay	ND	5.0	4	3.9
	soil	ND	25.0	4	1.0
	sludge	ND	125	4	7.2
	fly ash	7.4	7.4	3	7.6
	still bottom	ND	2500	2	-
1,2,3,7,8-PeCDF	clay	ND	5.0	4	6.1
	soil	ND	25.0	4	5.0
	sludge	ND	125	4	4.8
	fly ash	ND	46	2	-
	still bottom[3]	25600	28100	2	-
1,2,3,4,7,8-HxCDF	clay	ND	5.0	4	26
	soil	ND	25.0	4	6.8
	sludge	13.6	139	4	5.6
	fly ash	24.2	24.2	4	13.5
	still bottom	ND	2500	2	-

TABLE 5. (Continued)

Compound	Matrix[a]	Analyte level (ng/g) Native	Native + spike	N	Percent RSD
OCDF	clay	ND	-	-	-
	soil	ND	-	-	-
	sludge	192	317	4	3.3
	fly ash	ND	-	-	-
	still bottom	ND	-	-	-

[a]matrix types:

clay: pottery clay.

soil: Times Beach, Missouri, soil blended to form a homogeneous sample. This sample was analyzed as a performance evaluation sample for the Contract Laboratory Program (CLP) in April 1983. The results from EMSL-LV and 8 contract laboratories using the CLP protocol were 305.8 ng/g 2,3,7,8-TCDD with a standard deviation of 81.0.

fly ash: ash from a municipal incinerator; resource recovery ash No. 1.

still bottom: distillation bottoms (tar) from 2,4-dichlorophenol production.

sludge: sludge from cooling tower which received both creosote and pentachlorophenolic wastewaters.

Cleanup of clay, soil and fly ash samples was through alumina column only. (Carbon column not used.)

[b]ND - not detected at concentration injected (final volume 0.1 mL or greater).

[c]Estimated concentration out of calibration range of standards.

TABLE 6. RECOVERY DATA FOR REVISED METHOD 8280

Compound	Matrix[a]	Native[b] (ng/g)	Spiked[c] level (ng/g)	Mean percent recovery
2,3,7,8-TCDD	clay	ND	5.0	61.7
	soil	378	-	-
	sludge	ND	125	90.0
	fly ash	ND	46	90.0
	still bottom	487	-	-
1,2,3,4-TCDD	clay	ND	5.0	67.0
	soil	ND	25.0	60.3
	sludge	ND	125	73.1
	fly ash	38.5	46	105.6
	still bottom	ND	2500	93.8
1,3,6,8-TCDD	clay	ND	2.5	39.4
	soil	ND	25.0	64.0
	sludge	ND	125	64.5
	fly ash	19.1	46	127.5
	still bottom	227	2500	80.2
1,3,7,9-TCDD	clay	ND	2.5	68.5
	soil	ND	25.0	61.3
	sludge	ND	125	78.4
	fly ash	58.4	46	85.0
	still bottom	ND	2500	91.7
1,3,7,8-TCDD	clay	ND	5.0	68.0
	soil	ND	25.0	79.3
	sludge	ND	125	78.9
	fly ash	16.0	46	80.2
	still bottom	615	2500	90.5
1,2,7,8-TCDD	clay	ND	5.0	68.0
	soil	ND	25.0	75.3
	sludge	ND	125	80.4
	fly ash	2.6	46	90.4
	still bottom	ND	2500	88.4
1,2,8,9-TCDD	clay	ND	5.0	59.7
	soil	ND	25.0	60.3
	sludge	ND	125	72.8
	fly ash	ND	46	114.3
	still bottom	ND	2500	81.2

TABLE 6. (Continued)

Compound	Matrix[a]	Native[b] (ng/g)	Spiked[c] level (ng/g)	Mean percent recovery
1,2,3,4,7-PeCDD	clay	ND	5.0	58.4
	soil	ND	25.0	62.2
	sludge	ND	125	79.2
	fly ash	25.8	46	102.4
	still bottom	ND	2500	81.8
1,2,3,7,8-PeCDD	clay	ND	5.0	61.7
	soil	ND	25.0	68.4
	sludge	ND	125	81.5
	fly ash	ND	46	104.9
	still bottom	ND	2500	84.0
1,2,3,4,7,8-HxCDD	clay	ND	5.0	46.8
	soil	ND	25.0	65.0
	sludge	ND	125	81.9
	fly ash	ND	46	125.4
	still bottom	ND	2500	89.1
1,2,3,4,6,7,8-HpCDD	clay	ND	5.0	ND
	soil	ND	25.0	ND
	sludge[d]	8780	125	-
	fly ash	ND	-	-
	still bottom	ND	-	-
2,3,7,8-TCDD (C-13)	clay	ND	5.0	64.9
	soil	ND	25.0	78.8
	sludge	ND	125	78.6
	fly ash	ND	46	88.6
	still bottom	ND	2500	69.7
1,2,7,8-TCDF	clay	ND	5.0	65.4
	soil	ND	25.0	71.1
	sludge	ND	125	80.4
	fly ash	7.4	46	90.4
	still bottom	ND	2500	104.5
1,2,3,7,8-PeCDF	clay	ND	5.0	57.4
	soil	ND	25.0	64.4
	sludge	ND	125	84.8
	fly ash	ND	46	105.8
	still bottom	25600	2500	-

TABLE 6. (Continued)

Compound	Matrix[a]	Native[b] (ng/g)	Spiked[c] level (ng/g)	Mean percent recovery
1,2,3,4,7,8-HxCDF	clay	ND	5.0	54.2
	soil	ND	25.0	68.5
	sludge	13.6	125	82.2
	fly ash	24.2	46	91.0
	still bottom	ND	2500	92.9
OCDF	clay	ND	-	-
	soil	ND	-	-
	sludge	192	125	86.8
	fly ash	ND	-	-
	still bottom	ND	-	-

[a]matrix types:

clay: pottery clay.

soil: Times Beach, Missouri soil blended to form a homogeneous sample. This sample was analyzed as a performance evaluation sample for the Contract Laboratory Program (CLP) in April 1983. The results from EMSL-LV and 8 contract laboratories using the CLP protocol were 305.8 ng/g 2,3,7,8-TCDD with a standard deviation of 81.0.

fly ash: ash from a municipal incinerator: resource recovery ash No. 1.

still bottom: distillation bottoms (tar) from 2,4-dichlorophenol production.

sludge: sludge from cooling tower which received both creosote and pentachlorophenol wastewaters.

The clay, soil and fly ash samples were subjected to alumina column cleanup, no carbon column was used.

[b]Final volume of concentrate 0.1 mL or greater, ND means below quantification limit, 2 or more samples analyzed.

[c]Amount of analyte added to sample, 2 or more samples analyzed.

[d]Estimated concentration out of calibration range of standards.

TABLE 7. LINEAR RANGE AND VARIATIOIN OF RESPONSE FACTORS

Analyte	Linear range tested (pg)	n[b]	Mean RF	%RSD
1,2,7,8-TCDF[a]	50-6000	8	1.634	12.0
2,3,7,8-TCDD[a]	50-7000	7	0.721	11.9
2,3,7,8-TCDF	300-4000	5	2.208	7.9

[a]Response factors for these analytes were calculated using 2,3,7,8-TCDF as the internal standard. The response factors for 2,3,7,8-TCDF were calculated vs. $^{13}C_{12}$-1,2,3,4-TCDD.

[b]Each value of n represents a different concentration level.

TABLE 8. METHOD DETECTION LIMITS OF $^{13}C_{12}$ - LABELED PCDD'S and PCDF'S IN REAGENT WATER (PPT) AND ENVIRONMENTAL SAMPLES (PPB)

$^{13}C_{12}$-Labeled Analyte	Reagent Water[a]	Missouri Soil[b]	Fly-Ash[b]	Industrial Sludge[c]	Still-Bottom[d]	Fuel Oil[d]	Fuel Oil/Sawdust[b]
2,3,7,8-TCDD	0.44	0.17	0.07	0.82	1.81	0.75	0.13
1,2,3,7,8-PeCDD	1.27	0.70	0.25	1.34	2.46	2.09	0.18
1,2,3,6,7,8-HxCDD	2.21	1.25	0.55	2.30	6.21	5.02	0.36
1,2,3,4,6,7,8-HpCDD	2.77	1.87	1.41	4.65	4.59	8.14	0.51
OCDD	3.93	2.35	2.27	6.44	10.1	23.2	1.48
2,3,7,8-TCDF	0.63	0.11	0.06	0.46	0.26	0.48	0.40
1,2,3,7,8-PeCDF	1.64	0.33	0.16	0.92	1.61	0.80	0.43
1,2,3,4,7,8-HxCDF	2.53	0.83	0.30	2.17	2.27	2.09	2.22

[a] Sample size 1,000 mL.
[b] Sample size 10 g.
[c] Sample size 2 g.
[d] Sample size 1 g.
Note: The final sample-extract volume was 100 uL for all samples.

Matrix types used in MDL Study:

- Reagent water: distilled, deionized laboratory water.
- Missouri soil: soil blended to form a homogeneous sample.
- Fly-ash: alkaline ash recovered from the electrostatic precipitator of a coal-burning power plant.
- Industrial sludge: sludge from cooling tower which received creosotic and pentachlorophenolic wastewaters. Sample was ca. 70 percent water, mixed with oil and sludge.
- Still-bottom: distillation bottoms (tar) from 2,4-dichlorophenol production.
- Fuel oil: wood-preservative solution from the modified Thermal Process tanks. Sample was an oily liquid (>90 percent oil) containing no water.
- Fuel oil/Sawdust: sawdust was obtained as a very fine powder from the local lumber yard. Fuel oil (described above) was mixed at the 4 percent (w/w) level.

Procedure used for the Determination of Method Detection Limits was obtained from "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater" Appendix A, EPA-600/4-82-057, July 1982. Using this procedure, the method detection limit is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the value is above zero.

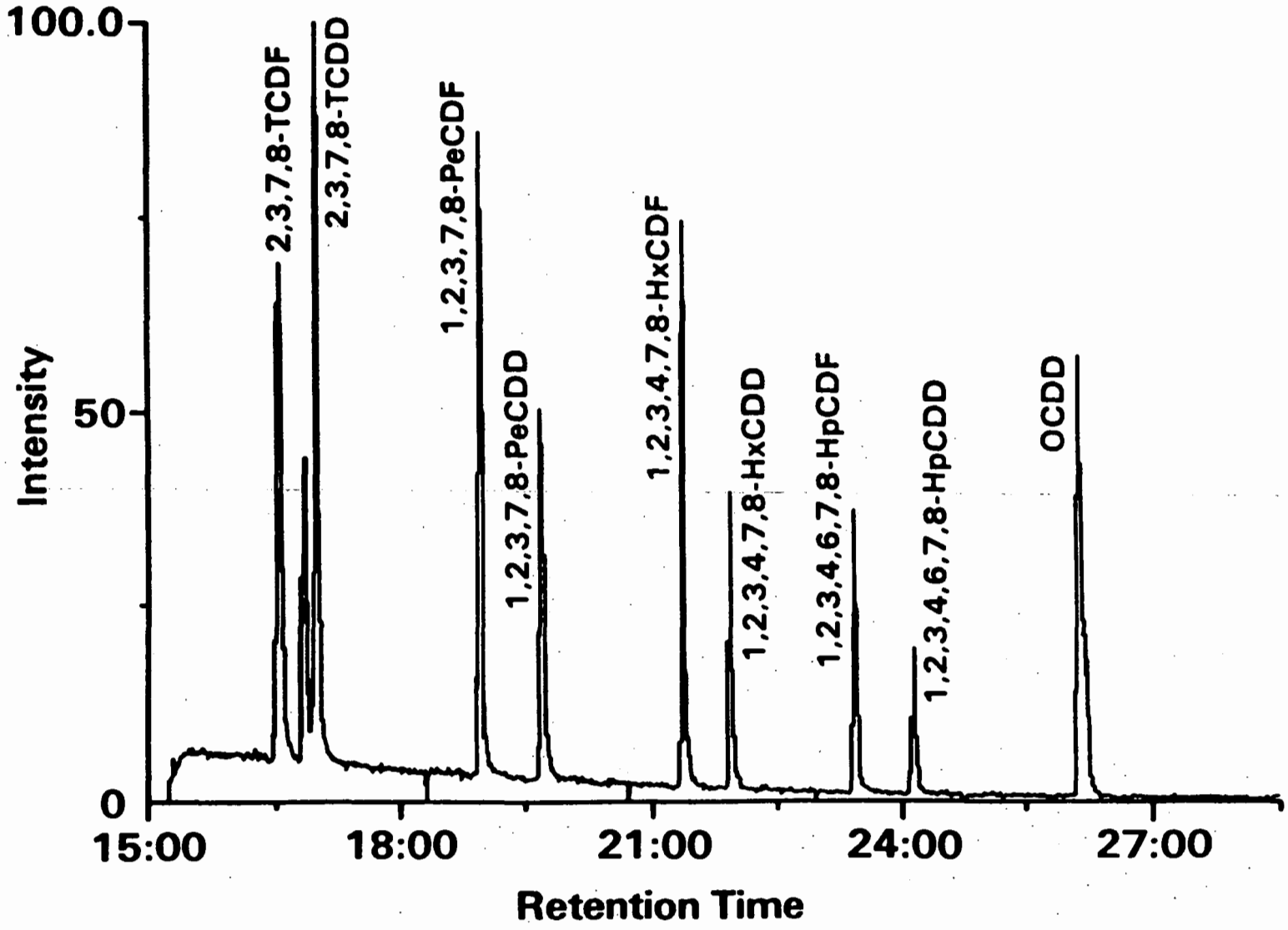
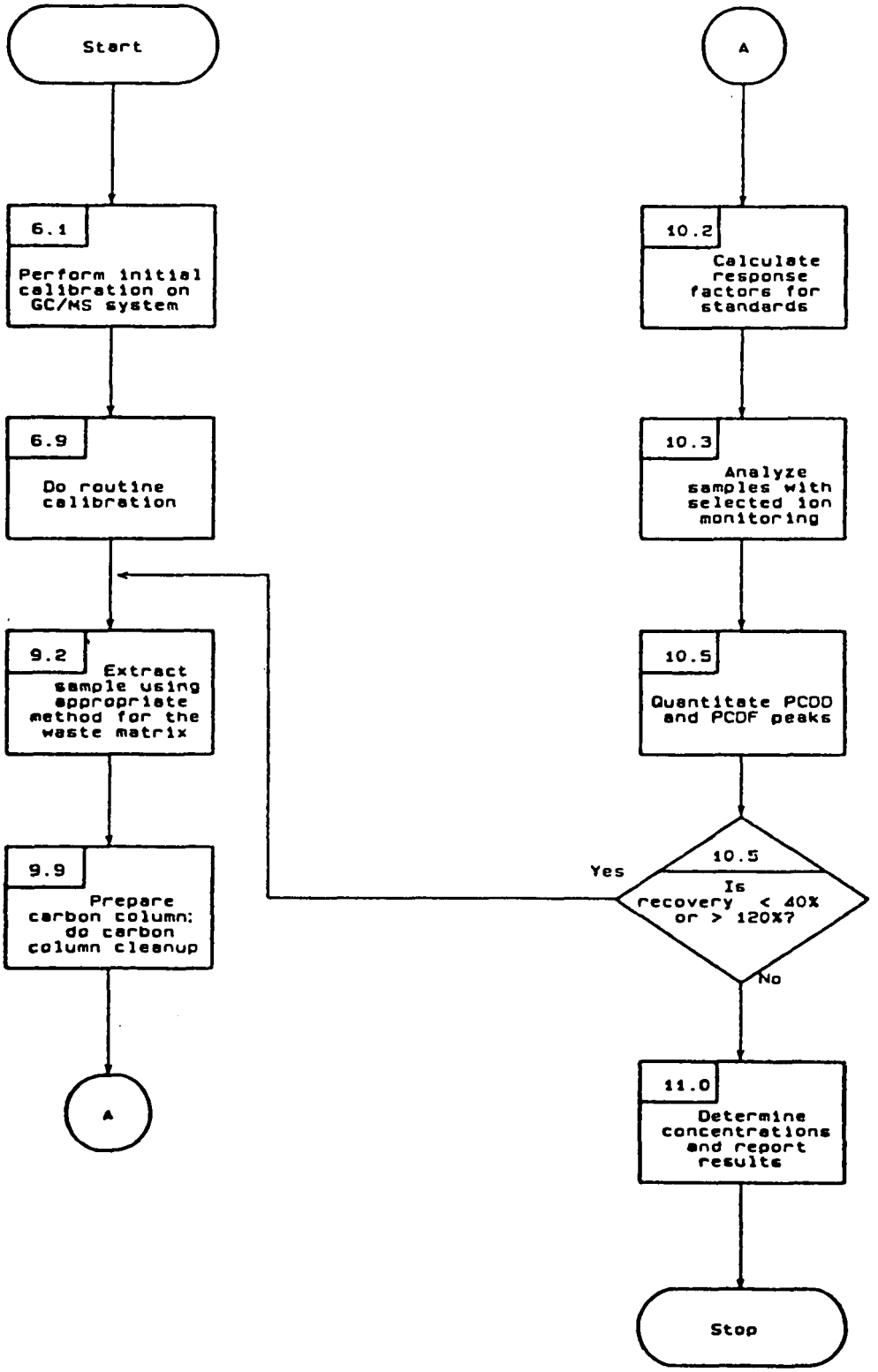


Figure 2. Mass Chromatogram of Selected PCDD and PCDF Congeners.


Start
6.1
Perform initial calibration on GC/MS system
6.9
Do routine calibration
9.2
Extract sample using appropriate method for the waste matrix
9.9
Prepare carbon column; do carbon column cleanup
A
A
10.2
Calculate response factors for standards
10.3
Analyze samples with selected ion monitoring
10.5
Quantitate PCDD and PCDF peaks
10.5
Is recovery < 40% or > 120%?
Yes
No
11.0
Determine concentrations and report results
Stop

APPENDIX A

SIGNAL-TO-NOISE DETERMINATION METHODS

MANUAL DETERMINATION

This method corresponds to a manual determination of the S/N from a GC/MS signal, based on the measurement of its peak height relative to the baseline noise. The procedure is composed of four steps as outlined below. (Refer to Figure 1 for the following discussion).

1. Estimate the peak-to-peak noise (N) by tracing the two lines (E_1 and E_2) defining the noise envelope. The lines should pass through the estimated statistical mean of the positive and the negative peak excursions as shown in Figure 1. In addition, the signal offset (O) should be set high enough such that negative-going noise (except for spurious negative spikes) is recorded.

2. Draw the line (C) corresponding to the mean noise between the segments defining the noise envelope.

3. Measure the height of the GC/MS signal (S) at the apex of the peak relative to the mean noise C. For noisy GC/MS signals, the average peak height should be measured from the estimated mean apex signal D between E_3 and E_4.

4. Compute the S/N.

This method of S/N measurement is a conventional, accepted method of noise measurement in analytical chemistry.

INTERACTIVE COMPUTER GRAPHICAL METHOD

This method calls for the measurement of the GC/MS peak area using the computer data system and Eq. 1:

$$S/N = \frac{A/t}{\frac{A_l/2t + A_r/2t}{2}}$$

where t is the elution time window (time interval, t_2-t_2, at the base of the peak used to measure the peak area A). (Refer to Figure 2, for the following discussion).

A_l and A_r correspond to the areas of the noise level in a region to the left (A_l) and to the right (A_r) of the GC peak of interest.

The procedure to determine the S/N is as follows:

1. Estimate the average negative peak excursions of the noise (i.e., the low segment-E_2-of the noise envelope). Line E_2 should pass through the estimated statistical mean of the negative-going noise excursions. As stated earlier, it is important to have the signal offset (0) set high enough such that negative-going noise is recorded.

2. Using the cross-hairs of the video display terminal, measure the peak area (A) above a baseline corresponding to the mean negative noise value (E_2) and between the time t_1 and t_2 where the GC/MS peak intersects the baseline, E_2. Make note of the time width $t=t_2-t_1$.

3. Following a similar procedure as described above, measure the area of the noise in a region to the left (A_l) and to the right (A_r) of the GC/MS signal using a time window twice the size of t, that is, 2 x t.

The analyst must sound judgement in regard to the proper selection of interference-free regions in the measurement of A_l and A_r. It is not recommended to perform these noise measurements (A_l and A_r) in remote regions exceeding ten time widths (10t).

4. Compute the S/N using Eq. 1.

NOTE: If the noise does not occupy at least 10 percent of the vertical axis (i.e., the noise envelope cannot be defined accurately), then it is necessary to amplify the vertical axis so that the noise occupies 20 percent of the terminal display (see Figure 3).

FIGURE CAPTIONS

Figure 1. Manual determination of S/N.
The peak height (S) is measured between the mean noise (lines C and D). These mean signal values are obtained by tracing the line between the baseline average noise extremes, E_1 and E_2, and between the apex average noise extremes, E_3 and E_4, at the apex of the signal. Note, it is imperative that the instrument's interface amplifier electronic's zero offset be set high enough such that negative-going baseline noise is recorded.

Figure 2. Interactive determination of S/N.
The peak area (A) is measured above the baseline average negative noise E_2 and between times t_1 and t_2. The noise is obtained from the areas A_1 and A_r measured to the left and to the right of the peak of interest using time windows T_1 and T_r (T_1=T_r=2t).

Figure 3. Interactive determination of S/N.
A) Area measurements without amplification of the vertical axis. Note that the noise cannot be determined accurately by visual means. B) Area measurements after amplification (10X) of the vertical axis so that the noise level occupies approximately 20 percent of the display, thus enabling a better visual estimation of the baseline noise, E_1, E_2, and C.

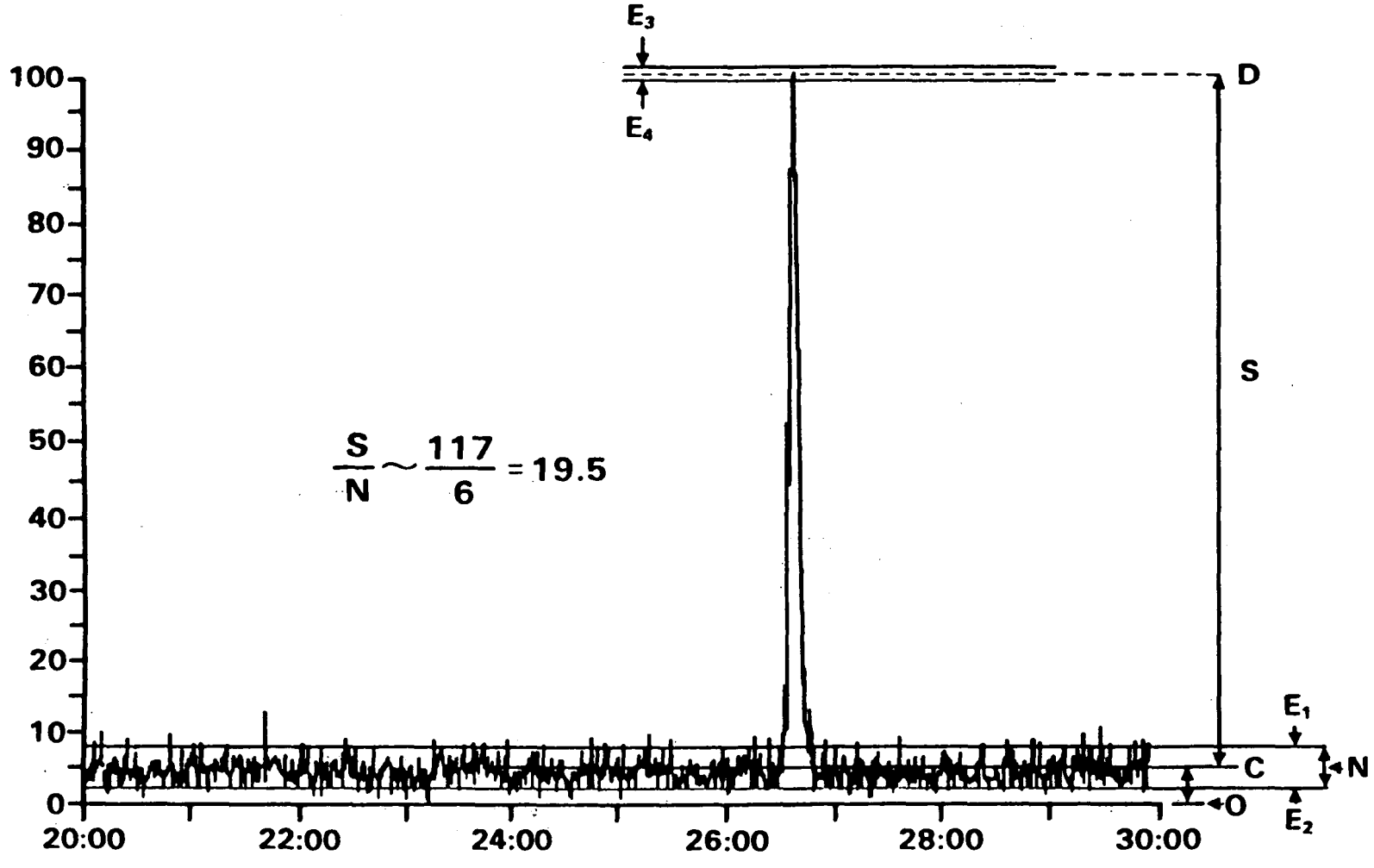


Figure 1. Manual Determination of S/N.

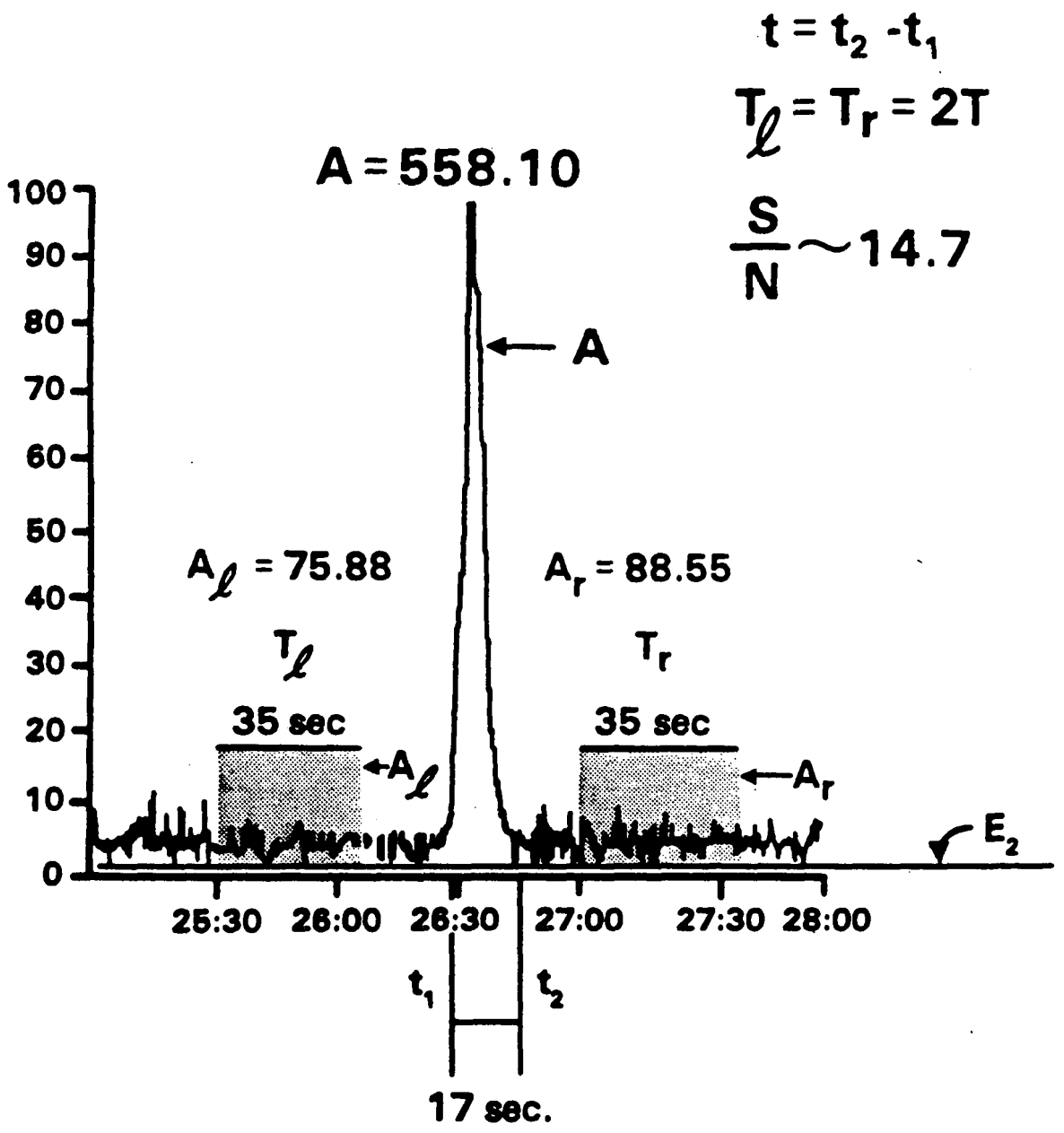


Figure 2. Interactive Determination of S/N.

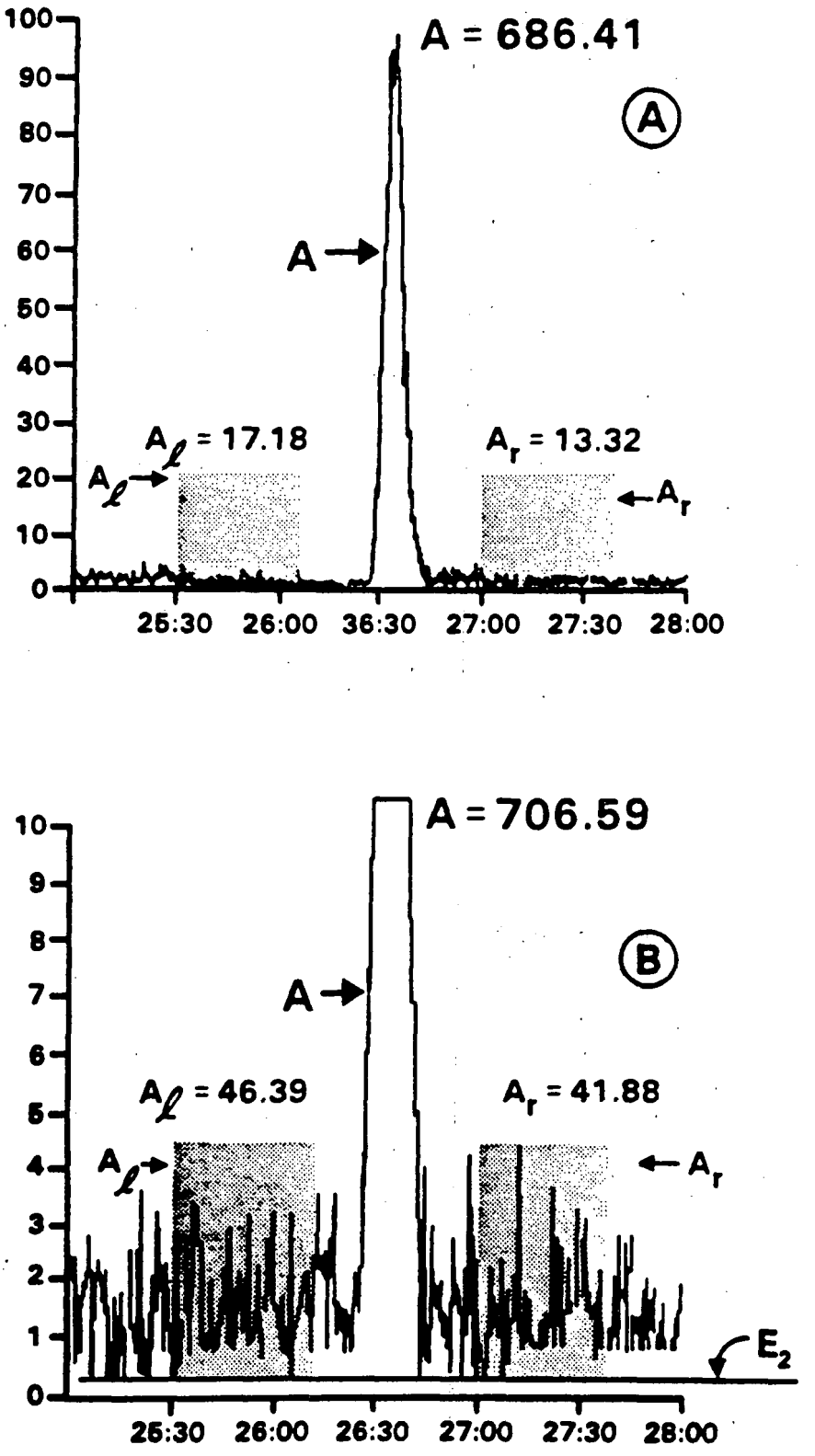


Figure 3. Interactive Determination of S/N.

APPENDIX B

RECOMMENDED SAFETY AND HANDLING PROCEDURES FOR PCDD'S/PCDF'S

1. The human toxicology of PCDD/PCDF is not well defined at present, although the 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in the course of laboratory animal studies. The 2,3,7,8-TCDD is a solid at room temperature, and has a relatively low vapor pressure. The solubility of this compound in water is only about 200 parts-per-trillion, but the solubility in various organic solvents ranges from about 0.001 perent to 0.14 percent. The physical properties of the 135 other tetra- through octa-chlorinated PCDD/PCDF have not been well established, although it is presumed that the physical properties of these congeners are generally similar to those of the 2,3,7,8-TCDD isomer. On the basis of the available toxicological and physical property data for TCDD, this compound, as well as the other PCDD and PCDF, should be handled only by highly trained personnel who are thoroughly versed in the appropriate procedures, and who understand the associated risks.

2. PCDD/PCDF and samples containing these are handled using essentially the same techniques as those employed in handling radioactive or infectious materials. Well-ventilated, controlled-access laboratories are required, and laboratory personel entering these laboratories should wear appropriate safety clothing, including disposable coveralls, shoe covers, gloves, and face and head masks. During analytical operations which may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters. Eye protection equipment (preferably full face shields) must be worn at all times while working in the analytical laboratory with PCDD/PCDF. Various types of gloves can be used by personnel, depending upon the analytical operation being accomplished. Latex gloves are generally utilized, and when handling samples thought to be particularly hazardous, an additional set of gloves are also worn beneath the latex gloves (for example, Playtex gloves supplied by American Scientific Products, Cat. No. 67216). Bench-tops and other work surfaces in the laboratory should be covered with plastic-backed absorbent paper during all analytical processing. When finely divided samples (dusts, soils, dry chemicals) are processed, removal of these from sample contaners, as well as other operations, including weighing, transferring, and mixing with solvents, should all be accomplished within a glove box. Glove boxes, hoods and the effluents from mechanical vacuum pumps and gas chromatographs on the mass spectrometers should be vented to the atmosphere preferably only after passing through HEPA particulate filters and vapor-sorbing charcoal.

3. All laboratory ware, safety clothing, and other items potentially contaminated with PCDD/PCDF in the course of analyses must be carefully secured and subjected to proper disposal. When feasible, liquid wastes are concentrated, and the residues are placed in approved steel hazardous waste drums fitted with heavy gauge polyethylene liners. Glass and combustible items are compacted using a dedicated trash compactor used only for hazardous waste materials and then placed in the same type of disposal drum. Disposal of accumulated wastes is periodically accomplished by high temperature incineration at EPA-aproved facilities.

4. Surfaces of laboratory benches, apparatus and other appropriate areas should be periodically subjected to surface wipe tests using solvent-wetted filter paper which is then analyzed to check for PCDD/PCDF contamination in the laboratory. Typically, if the detectable level of TCDD or TCDF from such a test is greater than 50 ng/m^2, this indicates the need for decontamination of the laboratory. A typical action limit in terms of surface contamination of the other PCDD/PCDF (summed) is 500 ng/m^2. In the event of a spill within the laboratory, absorbent paper is used to wipe up the spilled material and this is then placed into a hazardous waste drum. The contaminated surface is subsequently cleaned thoroughly by washing with appropriate solvents (methylene chloride followed by methanol) and laboratory detergents. This is repeated until wipe tests indicate that the levels of surface contamination are below the limits cited.

5. In the unlikely event that analytical personnel experience skin contact with PCDD/PCDF or samples containing these, the contaminated skin area should immediately be thoroughly scurbbed using mild soap and water. Personnel involved in any such accident should subsequently be taken to the nearest medical facility, preferably a facility whose staff is knowledgeable in the toxicology of chlorinated hydrocarbons. Again, disposal of contaminated clothing is accomplished by placing it in hazardous waste drums.

6. It is desirable that personnel working in laboratories where PCDD/PCDF are handled be given periodic physical examinations (at least yearly). Such examinations should include specialized tests, such as those for urinary porphyrins and for certain blood parameters which, based upon published clinical observations, are appropriate for persons who may be exposed to PCDD/PCDF. Periodic facial photographs to document the onset of dermatologic problems are also advisable.

DIOXIN SAMPLE DATA SUMMARY FORM 8280-1

LAB NAME _____ CONTRACT No._____

CASE No. _____

QUANTITY FOUND (ng/g)

SAMPLE NO.	FILE NAME	TCDD	PeCDD	HxCDD	HpCDD	OCDD

DATA RELEASE AUTHORIZED BY _____

Revision 0
Date September 1986

DIOXIN SAMPLE DATA SUMMARY FORM 8280-1

LAB NAME _____ CONTRACT No. _____

CASE No. _____

QUANTITY FOUND (ng/g)

SAMPLE NO.	FILE NAME	TCDF	PeCDF	HxCDF	HpCDF	OCDF

Revision 0
Date September 1986

DIOXIN SAMPLE DATA SUMMARY FORM 8280-1-W

LAB NAME _____ CONTRACT No. _____

CASE No. _____

QUANTITY FOUND (ug/L)

SAMPLE NO.	FILE NAME	TCDD	PeCDD	HxCDD	HpCDD	OCDD

DATA RELEASE AUTHORIZED BY _____

DIOXIN SAMPLE DATA SUMMARY FORM 8280-1-W

LAB NAME _____ CONTRACT No. _____

CASE No. _____

QUANTITY FOUND (ug/L)

SAMPLE NO.	FILE NAME	TCDF	PeCDF	HxCDF	HpCDF	OCDF

DIOXIN RAW SAMPLE DATA FORM 8280-2

LAB NAME _____ ANALYST(s) _____ CASE No. _____

SAMPLE No. _____ TYPE OF SAMPLE _____ CONTRACT No. _____

SAMPLE SIZE _____ % MOISTURE _____ FINAL EXTRACT VOLUME _____

EXTRACTION METHOD _____ ALIQUOT USED FOR ANALYSIS _____

CLEAN UP OPTION _____

CONCENTRATION FACTOR _____ DILUTION FACTOR _____

DATE EXTRACTED _____ DATA ANALYZED _____

VOLUME $^{13}C_{12}$-1,2,3,4-TCDD ADDED _____ TO SAMPLE VOLUME _____

VOLUME INJECTED _____ Wt $^{13}C_{12}$-1,2,3,4-TCDD ADDED _____

Wt $^{13}C_{12}$-2,3,7,8-TCDD ADDED _____ $^{13}C_{12}$-2,3,7,8-TCDD % RECOVERY _____

Wt $^{13}C_{12}$-2,3,7,8-OCDD ADDED _____ $^{13}C^{12}$-OCDD % RECOVERY _____

$^{13}C_{12}$-2,3,7,8-TCDD RRF _____ $^{13}C_{12}$-OCDD RRF _____

$^{13}C_{12}$-2,3,7,8-TCDD

AREA 332 _____ AREA 334 _____ RATIO 332/334 _____

$^{13}C_{12}$-OCDD AREA 470 _____ AREA 472 _____ RATIO 470/472 _____

RT 2,3,7,8-TCDD (Standard) _____ RT 2,3,7,8-TCDD (Sample) _____

$^{13}C_{12}$-2,3,7,8-TCDD - $^{13}C_{12}$-1,2,3,4-TCDD Percent Valley _____

Revision 0
Date September 1986

DIOXIN INITIAL CALIBRATION STANDARD DATA SUMMARY

FORM 8280-3

CASE No. _____

Lab Name _____ Contract No. _____

Date of Initial Calibration _____ Analyst(s)_____

Relative to $^{13}C_{12}$-2,3,7,8-TCDD_____ or $^{13}C_{12}$-1,2,3,^{4}-TCDD_____

CALIBRATION STANDARD	RRF 1	RRF 2	RRF 3	RRF 4	RRF 5	MEAN	%RSD
TCDD							
PeCDD							
HxCDD							
HpCDD							
OCDD							
TCDF							
PeCDF							
HxCDF							
HpCDF							
OCDF							

FORM 8280-3 (Continued)

CONCENTRATIONS IN PG/UL

	1	2	3	4	5
TCDD					
PeCDD					
HxCDD					
HpCDD					
OCDD					
TCDF					
PeCDF					
HxCDF					
HpCDF					
OCDF					

DIOXIN CONTINUING CALIBRATION SUMMARY

FORM 8280-4

CASE No. _____

Lab Name _____ Contract No. _____

Date of Initial Calibration _____ Analyst(s) _____

Relative to $^{13}C_{12}$-2,3,7,8-TCDD _____ or $^{13}C_{12}$-1,2,3,4-TCDD _____

COMPOUND	$\overline{RRF}$	RRF	%D
TCDD			
PeCDD			
HxCDD			
HpCDD			
OCDD			
TCDF			
PeCDF			
HxCDF			
HpCDF			
OCDF			

Revision 0
Date September 1986

DIOXIN RAW SAMPLE DATA FORM 8280-5-A

LAB NAME _____ ANALYST(s) _____ CASE No. _____

CONTRACT No. _____ SAMPLE No. _____

TCDD REQUIRED 320/322 RATIO WINDOW IS 0.65 - 0.89

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 322	AREA 320	AREA 257	320/ 322	CONFIRM AS TCDD Y/N	CONC.

TOTAL TCDD _____

TCDF REQUIRED 304/306 RATIO WINDOW IS 0.65 - 0.89

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 306	AREA 304	AREA 243	304/ 306	CONFIRM AS TCDD Y/N	CONC.

TOTAL TCDD _____

DIOXIN RAW SAMPLE DATA FORM 8280-5-B

LAB NAME _____ ANALYST(s) _____ CASE No. _____

CONTRACT No. _____ SAMPLE No. _____

PeCDD REQUIRED 320/322 RATIO WINDOW IS 0.55 - 0.75

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 356	AREA 358	AREA 354	AREA 293	358/ 356	CONFIRM AS PeCDD Y/N	CONC.

TOTAL PeCDD _____

PeCDF REQUIRED 342/340 RATIO WINDOW IS 0.55 - 0.75

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 340	AREA 342	AREA 338	AREA 277	342/ 340	CONFIRM AS PeCDF Y/N	CONC.

TOTAL PeCDF _____

Revision 0
Date September 1986

DIOXIN RAW SAMPLE DATA FORM 8280-5-C

LAB NAME _____ ANALYST(s) _____ CASE No._____

CONTRACT No._____ SAMPLE No._____

HxCDD REQUIRED 392/390 RATIO WINDOW IS 0.69 - 0.93

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 390	AREA 392	AREA 388	AREA 327	392/ 390	CONFIRM AS HxCDD Y/N	CONC.

TOTAL HxCDD _____

HxCDF REQUIRED 376/374 RATIO WINDOW IS 0.69 - 0.93

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 376	AREA 374	AREA 372	AREA 311	376/ 374	CONFIRM AS HxCDF Y/N	CONC.

TOTAL HxCDF _____

DIOXIN RAW SAMPLE DATA FORM 8280-5-D

LAB NAME _____ ANALYST(s) _____ CASE No._____

CONTRACT No._____ SAMPLE No._____

HpCDD REQUIRED 426/444 RATIO WINDOW IS 0.83 - 1.12

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 424	AREA 426	AREA 422	AREA 361	426/ 424	CONFIRM AS HpCDD Y/N	CONC.

TOTAL HpCDD _____

HpCDF REQUIRED 410/408 RATIO WINDOW IS 0.83 - 1.12

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 408	AREA 410	AREA 406	AREA 345	410/ 408	CONFIRM AS HpCDF Y/N	CONC.

TOTAL HpCDF _____

DIOXIN RAW SAMPLE DATA FORM 8280-5-E

LAB NAME _____ ANALYST(s) _____ CASE No._____

CONTRACT No. _____ SAMPLE No. _____

OCDD REQUIRED 458/460 RATIO WINDOW IS 0.75 - 1.01

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 460	AREA 458	AREA 395	458/ 460	CONFIRM AS OCDD Y/N	CONC.

TOTAL OCDD _____

OCDF REQUIRED 442/444 RATIO WINDOW IS 0.75 - 1.01

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 444	AREA 442	AREA 379	442/ 444	CONFIRM AS OCDF Y/N	CONC.

TOTAL OCDF _____

DIOXIN SYSTEM PERFORMANCE CHECK ANALYSIS FORM 8280-6

LAB NAME _____ CASE No. _____

BEGINNING DATE _____ TIME _____ CONTRACT No._____

ENDING DATE _____ TIME _____ ANALYST(s) _____

PC SOLUTION IDENTIFIER _____

ISOTOPIC RATIO CRITERIA MEASUREMENT

PCDD's	IONS RATIOED	RATIO AT BEGINNING OF 12 HOUR PERIOD	RATIO AT END OF 12 HOUR PERIOD	ACCEPTABLE WINDOW
Tetra	320/322			0.65-0.89
Penta	358/356			0.55-0.75
Hexa	392/390			0.69-0.93
Hepta	426/424			0.83-1.12
Octa	458/460			0.75-1.01
PCDF's				
Tetra	304/306			0.65-0.89
Penta	342-340			0.55-0.75
Hexa	376-374			0.69-0.93
Hepta	410/408			0.83-1.12
Octa	442/444			0.75-1.01

Ratios out of criteria

	Beginning	End
PCDD	_____ out of _____	_____ out of _____
PCDF	_____ out of _____	_____ out of _____

NOTE: One form is required for each 12 hour period samples are analyzed.

METHOD 8310

POLYNUCLEAR AROMATIC HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 Method 8310 is used to determine the concentration of certain polynuclear aromatic hydrocarbons (PAH) in ground water and wastes. Specifically, Method 8310 is used to detect the following substances:

Acenaphthene	Chrysene
Acenaphthylene	Dibenzo(a,h)anthracene
Anthracene	Fluoranthene
Benzo(a)anthracene	Fluorene
Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene
Benzo(b)fluoranthene	Naphthalene
Benzo(ghi)perylene	Phenanthrene
Benzo(k)fluoranthene	Pyrene

1.2 Use of Method 8310 presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds listed above, he must develop independent protocols for the verification of identity.

1.3 The method detection limits for each compound in reagent water are listed in Table 1. Table 2 lists the practical quantitation limit (PQL) for other matrices. The sensitivity of this method usually depends on the level of interferences rather than instrumental limitations. The limits of detection listed in Table 1 for the liquid chromatographic approach represent sensitivities that can be achieved in the absence of interferences. When interferences are present, the level of sensitivity will be lower.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2.0 SUMMARY OF METHOD

2.1 Method 8310 provides high performance liquid chromatographic (HPLC) conditions for the detection of ppb levels of certain polynuclear aromatic hydrocarbons. Prior to use of this method, appropriate sample extraction techniques must be used. A 5- to 25-uL aliquot of the extract is injected into an HPLC, and compounds in the effluent are detected by ultraviolet (UV) and fluorescence detectors.

2.2 If interferences prevent proper detection of the analytes of interest, the method may also be performed on extracts that have undergone cleanup using silica gel column cleanup (Method 3630).

TABLE 1. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY OF PAHs[a]

Compound	Retention time (min)	Column capacity factor (k')	Method Detection limit (ug/L)	
			UV	Fluorescence
Naphthalene	16.6	12.2	1.8	
Acenaphthylene	18.5	13.7	2.3	
Acenaphthene	20.5	15.2	1.8	
Fluorene	21.2	15.8	0.21	
Phenanthrene	22.1	16.6		0.64
Anthracene	23.4	17.6		0.66
Fluoranthrene	24.5	18.5		0.21
Pyrene	25.4	19.1		0.27
Benzo(a)anthracene	28.5	21.6		0.013
Chrysene	29.3	22.2		0.15
Benzo(b)fluoranthene	31.6	24.0		0.018
Benzo(k)fluoranthene	32.9	25.1		0.017
Benzo(a)pyrene	33.9	25.9		0.023
Dibenzo(a,h)anthracene	35.7	27.4		0.030
Benzo(ghi)perylene	36.3	27.8		0.076
Indeno(1,2,3-cd)pyrene	37.4	28.7		0.043

[a] HPLC conditions: Reverse phase HC-ODS Sil-X, 5 micron particle size, in a 250-mm x 2.6-mm I.D. stainless steel column. Isocratic elution for 5 min using acetonitrile/water (4:6)(v/v), then linear gradient elution to 100% acetonitrile over 25 min at 0.5 mL/min flow rate. If columns having other internal diameters are used, the flow rate should be adjusted to maintain a linear velocity of 2 mm/sec.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method Detection Limit (Table 1) X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source. Although a general cleanup technique is provided as part of this method, individual samples may require additional cleanup approaches to achieve the sensitivities stated in Table 1.

3.3 The chromatographic conditions described allow for a unique resolution of the specific PAH compounds covered by this method. Other PAH compounds, in addition to matrix artifacts, may interfere.

4.0 APPARATUS AND MATERIALS

4.1 Kuderna-Danish (K-D) apparatus:

4.1.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.1.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.1.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.1.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.2 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.3 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.4 Syringe: 5-mL.

4.5 High pressure syringes.

4.6 HPLC apparatus:

4.6.1 **Gradient pumping system:** Constant flow.

4.6.2 **Reverse phase column:** HC-ODS Sil-X, 5-micron particle size diameter, in a 250-mm x 2.6-mm I.D. stainless steel column (Perkin Elmer No. 089-0716 or equivalent).

4.6.3 **Detectors:** Fluorescence and/or UV detectors may be used.

4.6.3.1 Fluorescence detector: For excitation at 280-nm and emission greater than 389-nm cutoff (Corning 3-75 or equivalent). Fluorometers should have dispersive optics for excitation and can utilize either filter or dispersive optics at the emission detector.

4.6.3.2 UV detector: 254-nm, coupled to the fluorescence detector.

4.6.4 **Strip-chart recorder:** compatible with detectors. A data system for measuring peak areas and retention times is recommended.

4.7 Volumetric flasks: 10-, 50-, and 100-mL.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2 Acetonitrile: HPLC quality, distilled in glass.

5.3 Stock standard solutions:

5.3.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in acetonitrile and diluting to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.3.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.4 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared through dilution of the stock standards with acetonitrile. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the HPLC. Calibration standards must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.5 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.5.1 Prepare calibration standards at a minimum of five concentration levels for each analyte as described in Paragraph 5.4.

5.5.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with acetonitrile.

5.5.3 Analyze each calibration standard according to Section 7.0.

5.6 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (if necessary), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two surrogates (e.g., decafluorobiphenyl or other PAHs not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. Deuterated analogs of analytes should not be used as surrogates for HPLC analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and must be analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550. To achieve maximum sensitivity with this method, the extract must be concentrated to 1 mL.

7.1.2 Prior to HPLC analysis, the extraction solvent must be exchanged to acetonitrile. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.2.2 Increase the temperature of the hot water bath to 95-100°C. Momentarily remove the Snyder column, add 4 mL of acetonitrile, a new boiling chip, and attach a two-ball micro-Snyder column. Concentrate the extract using 1 mL of acetonitrile to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 15-20 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.2.3 When the apparatus is cool, remove the micro-Snyder column and rinse its lower joint into the concentrator tube with about 0.2 mL of acetonitrile. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 1.0 mL. Stopper the concentrator tube and store refrigerated at 4°C, if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with HPLC analysis if further cleanup is not required.

7.2 HPLC conditions (Recommended):

7.2.1 Using the column described in Paragraph 4.6.2: Isocratic elution for 5 min using acetonitrile/water (4:6)(v/v), then linear gradient elution to 100% acetonitrile over 25 min at 0.5 mL/min flow rate. If columns having other internal diameters are used, the flow rate should be adjusted to maintain a linear velocity of 2 mm/sec.

7.3 Calibration:

7.3.1 Refer to Method 8000 for proper calibration procedures. The procedure of internal or external standard calibration may be used. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.2 Assemble the necessary HPLC apparatus and establish operating parameters equivalent to those indicated in Section 7.2.1. By injecting calibration standards, establish the sensitivity limit of the detectors and the linear range of the analytical systems for each compound.

7.3.3 Before using any cleanup procedure, the analyst should process a series of calibration standards through the procedure to confirm elution patterns and the absence of interferences from the reagents.

7.4 HPLC analysis:

7.4.1 Table 1 summarizes the estimate retention times of PAHs determinable by this method. Figure 1 is an example of the separation achievable using the conditions given in Paragraph 7.2.1.

Column: HC-ODS SIL-X
Mobile Phase: 40% to 100% Acetonitrile in Water
Dectector: Fluorescence

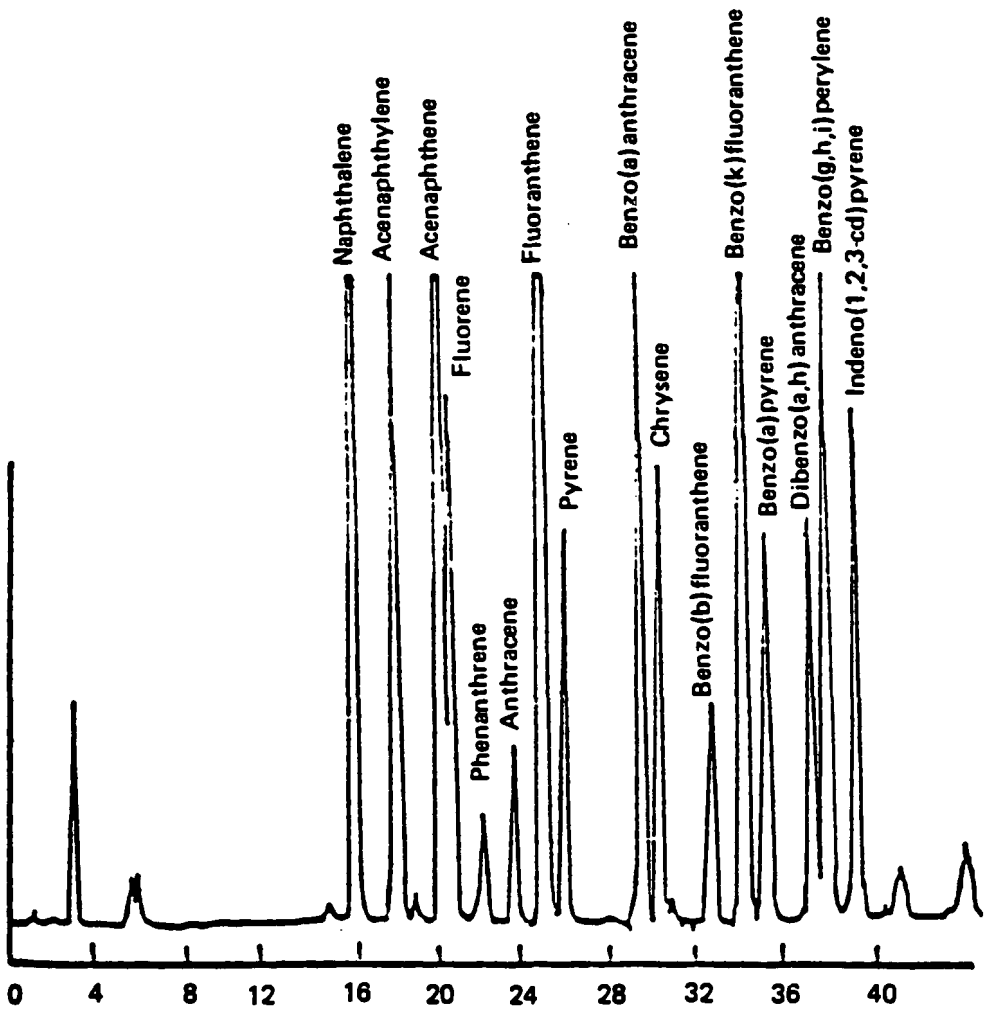


Figure 1. Liquid chromatogram of polynuclear aromatics.

7.4.2 If internal standard calibration is to be performed, add 10 uL of internal standard to the sample prior to injection. Inject 2-5 uL of the sample extract with a high-pressure syringe or sample injection loop. Record the volume injected to the nearest 0.1 uL, and the resulting peak size, in area units or peak heights. Re-equilibrate the HPLC column at the initial gradient conditions for at least 10 min between injections.

7.4.3 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Section 7.8 of Method 8000 for calculation equations.

7.4.4 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

7.4.5 If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

7.5 Cleanup:

7.5.1 Cleanup of the acetonitrile extract takes place using Method 3630 (Silica Gel Cleanup). Specific instructions for cleanup of the extract for PAHs is given in Section 7.1 of Method 3630.

7.5.2 Following cleanup, analyze the samples using HPLC as described in Section 7.4.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method used. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Mandatory quality control to validate the HPLC system operation is found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 ug/mL; acenaphthylene, 100 ug/mL; acenaphthene, 100 ug/mL; fluorene, 100 ug/mL; phenanthrene, 100 ug/mL; anthracene, 100 ug/mL; benzo(k)fluoranthene, 5 ug/mL; and any other PAH at 10 ug/mL.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 The method was tested by 16 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 0.1 to 425 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 4.

9.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 8 x MDL to 800 x MDL with the following exception: benzo(ghi)perylene recovery at 80 x and 800 x MDL were low (35% and 45%, respectively).

9.3 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters, Category 9 - PAHs," Report for EPA Contract 68-03-2624 (in preparation).

2. Sauter, A.D., L.D. Betowski, T.R. Smith, V.A. Strickler, R.G. Beimer, B.N. Colby, and J.E. Wilkinson, "Fused Silica Capillary Column GC/MS for the Analysis of Priority Pollutants," Journal of HRC&CC 4, 366-384, 1981.

3. "Determination of Polynuclear Aromatic Hydrocarbons in Industrial and Municipal Wastewaters," EPA-600/4-82-025, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, September 1982.

4. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

5. "EPA Method Validation Study 20, Method 610 (Polynuclear Aromatic Hydrocarbons)," Report for EPA Contract 68-03-2624 (in preparation).

6. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

7. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

TABLE 3. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range p, p_s (%)
Acenaphthene	100	40.3	D-105.7	D-124
Acenaphthylene	100	45.1	22.1-112.1	D-139
Anthracene	100	28.7	11.2-112.3	D-126
Benzo(a)anthracene	10	4.0	3.1-11.6	12-135
Benzo(a)pyrene	10	4.0	0.2-11.0	D-128
Benzo(b)fluoranthene	10	3.1	1.8-13.8	6-150
Benzo(ghi)perylene	10	2.3	D-10.7	D-116
Benzo(k)fluoranthene	5	2.5	D-7.0	D-159
Chrysene	10	4.2	D-17.5	D-199
Dibenzo(a,h)anthracene	10	2.0	0.3-10.0	D-110
Fluoranthene	10	3.0	2.7-11.1	14-123
Fluorene	100	43.0	D-119	D-142
Indeno(1,2,3-cd)pyrene	10	3.0	1.2-10.0	D-116
Naphthalene	100	40.7	21.5-100.0	D-122
Phenanthrene	100	37.7	8.4-133.7	D-155
Pyrene	10	3.4	1.4-12.1	D-140

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

p, p_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 610. These criteria are based directly upon the method performance data in Table 3. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 3.

TABLE 4. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Acenaphthene	0.52C+0.54	0.39$\bar{X}$+0.76	0.53$\bar{X}$+1.32
Acenaphthylene	0.69C-1.89	0.36$\bar{X}$+0.29	0.42$\bar{X}$+0.52
Anthracene	0.63C-1.26	0.23$\bar{X}$+1.16	0.41$\bar{X}$+0.45
Benzo(a)anthracene	0.73C+0.05	0.28$\bar{X}$+0.04	0.34$\bar{X}$+0.02
Benzo(a)pyrene	0.56C+0.01	0.38$\bar{X}$-0.01	0.53$\bar{X}$-0.01
Benzo(b)fluoranthene	0.78C+0.01	0.21$\bar{X}$+0.01	0.38$\bar{X}$-0.00
Benzo(ghi)perylene	0.44C+0.30	0.25$\bar{X}$+0.04	0.58$\bar{X}$+0.10
Benzo(k)fluoranthene	0.59C+0.00	0.44$\bar{X}$-0.00	0.69$\bar{X}$+0.10
Chrysene	0.77C-0.18	0.32$\bar{X}$-0.18	0.66$\bar{X}$-0.22
Dibenzo(a,h)anthracene	0.41C-0.11	0.24$\bar{X}$+0.02	0.45$\bar{X}$+0.03
Fluoranthene	0.68C+0.07	0.22$\bar{X}$+0.06	0.32$\bar{X}$+0.03
Fluorene	0.56C-0.52	0.44$\bar{X}$-1.12	0.63$\bar{X}$-0.65
Indeno(1,2,3-cd)pyrene	0.54C+0.06	0.29$\bar{X}$+0.02	0.42$\bar{X}$+0.01
Naphthalene	0.57C-0.70	0.39$\bar{X}$-0.18	0.41$\bar{X}$+0.74
Phenanthrene	0.72C-0.95	0.29$\bar{X}$+0.05	0.47$\bar{X}$-0.25
Pyrene	0.69C-0.12	0.25$\bar{X}$+0.14	0.42$\bar{X}$-0.00

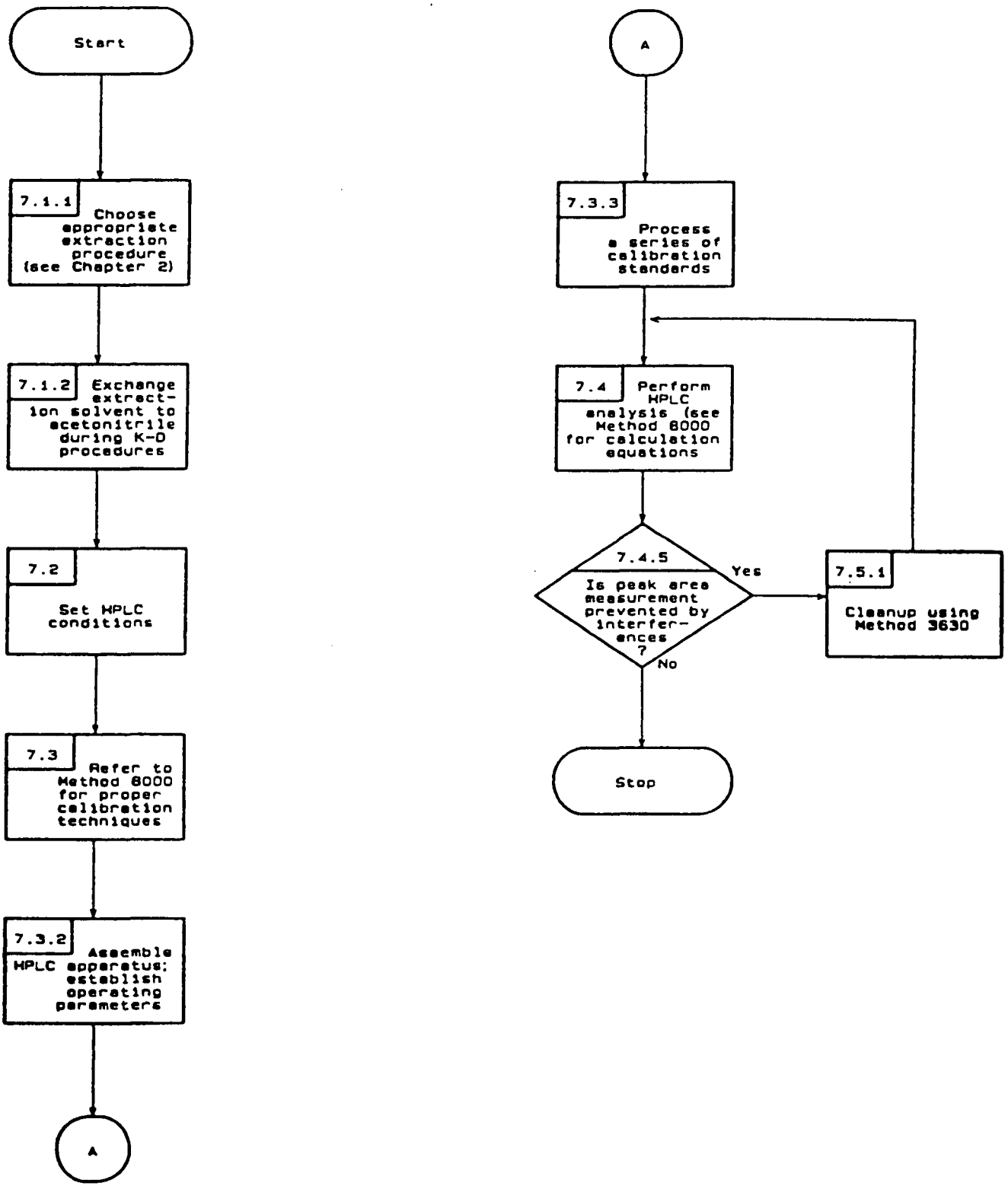
x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.


Start
7.1.1 Choose appropriate extraction procedure (see Chapter 2)
7.1.2 Exchange extraction solvent to acetonitrile during K-D procedures
7.2 Set HPLC conditions
7.3 Refer to Method 8000 for proper calibration techniques
7.3.2 Assemble HPLC apparatus; establish operating parameters
A
A
7.3.3 Process a series of calibration standards
7.4 Perform HPLC analysis (see Method 8000 for calculation equations
7.4.5 Is peak area measurement prevented by interferences ?
Yes
No
7.5.1 Cleanup using Method 3630
Stop

4.4 MISCELLANEOUS SCREENING METHODS

METHOD 3810

HEADSPACE

1.0 SCOPE AND APPLICATION

1.1 Method 3810 was formerly Method 5020 in the second edition of this manual.

1.2 Method 3810 is a static headspace technique for extracting volatile organic compounds from samples. It is a simple method that allows large numbers of samples to be screened in a relatively short period of time. It is ideal for screening samples prior to using the purge-and-trap method. Detection limits for this method may vary widely among samples because of the large variability and complicated matrices of waste samples. The method works best for compounds with boiling points of less than 125°C. The sensitivity of this method will depend on the equilibria of the various compounds between the vapor and dissolved phases.

1.3 Due to the variability of this method, this procedure is recommended for use only as a screening procedure for other, more accurate determinative methods (Methods 8010, 8015, 8020, 8030, and 8240).

2.0 SUMMARY OF METHOD

2.1 The sample is collected in sealed glass containers and allowed to equilibrate at 90°C. A sample of the headspace gas is withdrawn with a gas-tight syringe for screening analysis using the conditions specified in one of the GC or GC/MS determinative methods (8010, 8015, 8020, 8030, or 8240).

3.0 INTERFERENCES

3.1 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with reagent water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water. It may be necessary to wash out the syringe with detergent, rinse with distilled water, and dry in a 105°C oven between analyses.

3.3 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific determinative method for appropriate apparatus and materials.

4.2 Vials: 125-mL Hypo-Vials (Pierce Chemical Co., #12995, or equivalent), four each.

4.3 Septa: Tuf-Bond (Pierce #12720 or equivalent).

4.4 Seals: Aluminum (Pierce #13214l or equivalent).

4.5 Crimper: Hand (Pierce #13212 or equivalent).

4.6 Syringe: 5-mL, gas-tight with shutoff valve and chromatographic needles.

4.7 Microsyringe: 250- or 500-uL.

4.8 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

5.0 REAGENTS

5.1 Refer to the specific determinative method and Method 8000 for preparation of calibration standards.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Gas chromatographic conditions and Calibration: Refer to the specific determinative method for GC operating conditions and to Method 8000, Section 7.4, for calibration procedures.

7.2 Sample preparation:

7.2.1 Place 10.0 g of a well-mixed waste sample into each of two separate 125-mL septum-seal vials.

7.2.2 Dose one sample vial through the septum with 200 uL of a 50 ng/uL calibration standard containing the compounds of interest. Label this "1-ppm spike."

7.2.3 Dose a separate (empty) 125-mL septum seal vial with 200 uL of the same 50 ng/uL calibration standard. Label this "1-ppm standard."

7.2.4 Place the sample, 1-ppm-spike, and 1-ppm-standard vials into a 90°C water bath for 1 hr. Store the remaining sample vial at 4.0°C for possible future analysis.

7.3 Sample analysis:

7.3.1 While maintaining the vials at 90°C, withdraw 2 mL of the headspace gas with a gas-tight syringe and analyze by direct injection into a GC. The GC should be operated using the same GC conditions listed in the method being screened (8010, 8015, 8020, 8030, or 8240).

7.3.2 Analyze the 1-ppm standard and adjust instrument sensitivity to give a minimum response of at least 2 times the background. Record retention times (RT) and peak areas of compounds of interest.

7.3.3 Analyze the 1-ppm spiked sample in the same manner. Record RTs and peak areas.

7.3.4 Analyze the undosed sample as in Paragraph 7.3.3.

7.3.5 Use the results obtained to determine if the sample requires dilution or methanolic extraction as indicated in Method 5030.

8.0 QUALITY CONTROL

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 Standard quality assurance practices should be used with this method. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 ug/g of sample, then the sensitivity of the instrument should be increased.

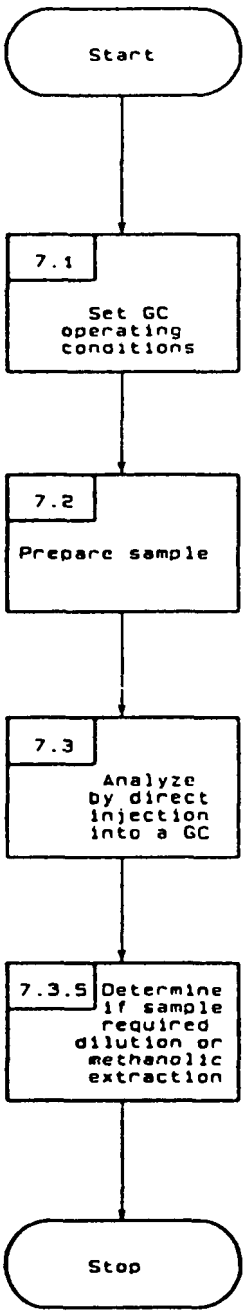
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Hachenberg, H. and A. Schmidt, Gas Chromatographic Headspace Analysis, Philadelphia: Hayden & Sons Inc., 1979.

2. Friant, S.L. and I.H. Suffet, "Interactive Effects of Temperature, Salt Concentration and pH on Headspace Analysis for Isolating Volatile Trace Organics in Aqueous Environmental Samples," Anal. Chem. 51, 2167-2172, 1979.


Start
7.1
Set GC operating conditions
7.2
Prepare sample
7.3
Analyze by direct injection into a GC
7.3.5
Determine if sample required dilution or methanolic extraction
Stop

METHOD 3820

HEXADECANE EXTRACTION AND SCREENING OF PURGEABLE ORGANICS

1.0 SCOPE AND APPLICATION

1.1 This method is a screening procedure for use with purge-and-trap GC or GC/MS. The results of this analysis are purely qualitative and should not be used as an alternative to more detailed and accurate quantitation methods.

2.0 SUMMARY OF METHOD

2.1 An aliquot of sample is extracted with hexadecane and then analyzed by GC/FID. The results of this analysis will indicate whether the sample requires dilution or methanolic extraction prior to purge-and-trap GC or GC/MS analysis.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, and glassware. All these materials must be routinely demonstrated to be free from contaminants by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from sample to sample depending upon the nature and diversity of the water being sampled.

3.2 The flame ionization detector varies considerably in sensitivity when comparing aromatics and halogenated methanes and ethanes. Halomethanes are approximately 20x less sensitive than aromatics and haloethanes approximately 10x less sensitive. Low-molecular-weight, water-soluble solvents (e.g., alcohols and ketones) will not extract from the water, and therefore will not be detected by GC/FID.

4.0 APPARATUS AND MATERIALS

4.1 Balance: Analytical, capable of accurately weighing 0.0001 gm.

4.2 Gas Chromatograph: An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder (or equivalent). A data system is recommended for measuring peak heights and/or peak areas.

4.2.1 **Detector:** Flame ionization (FID).

4.2.2 **GC column:** 3-m x 2-mm I.D. glass column packed with 10% OV-101 on 100/120 mesh Chromosorb W-HP (or equivalent). The column temperature should be programmed from 80°C to 280°C at 16°C/min and held at 280°C for 10 min.

4.3 Centrifuge: Capable of accommodating 50-mL glass tubes.

4.4 Vials and caps: 2-mL for GC autosampler.

4.5 Volumetric flasks: 10- and 50-mL with ground-glass stopper or Teflon-lined screw-cap.

4.6 Centrifuge tubes: 50-mL with ground-glass stopper or Teflon-lined screw-cap.

4.7 Pasteur pipets: Disposable.

4.8 Bottles: Teflon-sealed screw-cap.

5.0 REAGENTS

5.1 Hexadecane and methanol: Pesticide quality or equivalent.

5.2 Reagent water: Reagent water is defined as water in which an interference is not observed at the method detection limit of each parameter of interest.

5.3 Stock standard solutions (1.00 ug/uL): Stock standard solutions can be purchased as certified solutions or can be prepared from pure standard materials.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 grams of pure material. Dissolve the material in methanol in a 10-mL volumetric flask and dilute to volume (larger volumes may be used at the convenience of the analyst). If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially available stock standards may be used if they are certified by the manufacturer.

5.3.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. These standards should be checked frequently for signs of degradation or evaporation.

5.4 Standard mixture #1: Standard mixture #1 should contain benzene, toluene, ethyl benzene, and xylene. Prepare a stock solution containing these compounds as described in Paragraph 5.3 and then prepare a working standard (through dilution) in which the concentration of each compound in the standard is 100 ng/uL in methanol.

5.5 Standard mixture #2: Standard mixture #2 should contain n-nonane and n-dodecane. Prepare a stock solution containing these compounds as described in Paragraph 5.3. Dilute the stock standard with methanol so that the concentration of each compound is 100 ng/uL.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sample preparation:

7.1.1 Water:

7.1.1.1 Allow the contents of the 40-mL sample vial to come to room temperature. Quickly transfer the contents of the 40-mL vial to a 50-mL volumetric flask. Immediately add 2.0 mL of hexadecane, cap the flask, and shake the contents vigorously for 1 min. Let phases separate. Open the flask and add sufficient reagent water to bring the hexadecane layer into the neck of the flask.

7.1.1.2 Transfer approximately 1 mL of the hexadecane layer to a 2.0-mL GC vial. If an emulsion is present after shaking the sample, break it by:

1. pulling the emulsion through a small plug of Pyrex glass wool packed in a pipet, or

2. transferring the emulsion to a centrifuge tube and centrifuging for several min.

7.1.2 Standards:

7.1.2.1 Add 200 uL of the working standard mixtures #1 and #2 to separate 40-mL portions of reagent water. Follow the instructions in Sections 7.1.1.1 and 7.1.1.2 with the immediate addition of 2.0 mL of hexadecane.

7.1.3 Sediment/Soil:

7.1.3.1 Add approximately 10 g of sample (wet weight) to 40 mL of reagent water in a 50-mL centrifuge tube. Cap and shake vigorously for 1 min. Centrifuge the sample briefly. Quickly transfer the supernatant water to a 50-mL volumetric flask.

7.1.3.2 Follow the instructions given in Sections 7.1.1.1 and 7.1.1.2, starting with the addition of 2.0 mL of hexadecane.

7.2 Analysis:

7.2.1 Calibration:

7.2.1.1 External standard calibration: The GC/FID must be calibrated each 12-hour shift for half of full-scale response when injecting 1-5 uL of each extracted standard mixture #1 and #2 (Paragraphs 5.4 and 5.5).

7.2.2 **GC/FID analysis:** Inject the same volume of hexadecane extract for the sample under investigation as was used to perform the external standard calibration. The GC conditions used for the standards analysis must also be the same as those used to analyze the samples.

7.2.3 **Interpretation of the GC/FID chromatograms:** There are two options for interpretation of the GC/FID results.

7.2.3.1 Option A: The standard mixture #1 is used to calculate an approximate concentration of the aromatics in the sample. Use this information to determine the proper dilution for purge-and-trap if the sample is a water. If the sample is a sediment/soil, use this information to determine which GC/MS purge-and-trap method (low- or high-level) should be used. If aromatics are absent from the sample or obscured by higher concentrations of other purgeables, use Option B.

7.2.3.2 Option B: The response of standard mixture #2 is used to determine which purge-and-trap method should be used for analyzing a sample. All purgeables of interest have retention times less than the n-dodecane retention time. A dilution factor (Paragraph 7.2.4.1.3) may be calculated for water samples, and an X factor (Paragraph 7.2.4.2.3) for soil/sediment samples, to determine whether the low- or high-level purge-and-trap procedure should be used.

7.2.4 Analytical decision point:

7.2.4.1 Water samples: Compare the hexadecane sample extract chromatograms against an extracted standard chromatogram.

7.2.4.1.1 If no peaks are noted, analyze a 5-mL water sample by the purge-and-trap method.

7.2.4.1.2 If peaks are present prior to the n-dodecane peak and aromatics are distinguishable, follow Option A (Paragraph 7.2.3.1).

7.2.4.1.3 If peaks are present prior to the n-dodecane but the aromatics are absent or indistinguishable, Option B should be used as follows: If all peaks (prior to n-dodecane) are $<3\%$ of the n-nonane, analyze 5 mL of water sample by the purge-and-trap method. If any peak is $>3\%$ of the n-nonane, measure the area of the major peak and calculate the necessary dilution factor as follows:

$$\text{dilution factor} = 50 \times \frac{\text{area of major peak in sample}}{\text{peak area of n-nonane}}$$

The water sample should be diluted using the calculated factor just prior to purge-and-trap GC or GC/MS analysis.

7.2.4.2 **Soil/sediment samples:** Compare the hexadecane sample extract chromatograms against an extracted standard chromatogram.

7.2.4.2.1 If no peaks are noted, analyze a 5-g sample by the low-level purge-and-trap procedure.

7.2.4.2.2 If peaks are present prior to the n-dodecane and aromatics are distinguishable, follow Option A using the concentration information given in Table 1 to determine whether to analyze the sample by a low- or high-level purge-and-trap technique.

7.2.4.2.3 If peaks are present prior to n-dodecane but aromatics are absent or indistinguishable, use Option B. Calculate an X factor for the sample using the following equation:

$$X \text{ factor} = \frac{\text{area of major peak in sample}}{\text{area of n-nonane}}$$

Use the information provided in Table 1 to determine how the sample should be handled for GC/MS analysis.

7.2.4.2.4 If a high-level method is indicated, the information provided in Table 2 can be used to determine the volume of methanol extract to add to 5 mL of reagent water for analysis (see Methods 5030 and 8240 for methanolic extraction procedure).

8.0 QUALITY CONTROL

8.1 It is recommended that a reagent blank be analyzed by this screening procedure to ensure that no laboratory contamination exists. A blank should be performed for each set of samples undergoing extraction and screening.

9.0 METHOD PERFORMANCE

9.1 No data available.

10.0 REFERENCES

1. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

TABLE 1. DETERMINATION OF GC/MS PURGE-AND-TRAP METHOD

X Factor	Approximate Concentration Range [a]	Analyze by
0-1.0	0-1,000 ug/kg	Low-level method
>1.0	>1,000 ug/kg	High-level method

[a] This concentration range is based upon the response of aromatics to GC/FID. The concentration for halomethanes is 20x higher, and haloethanes 10x higher, when comparing GC/FID responses.

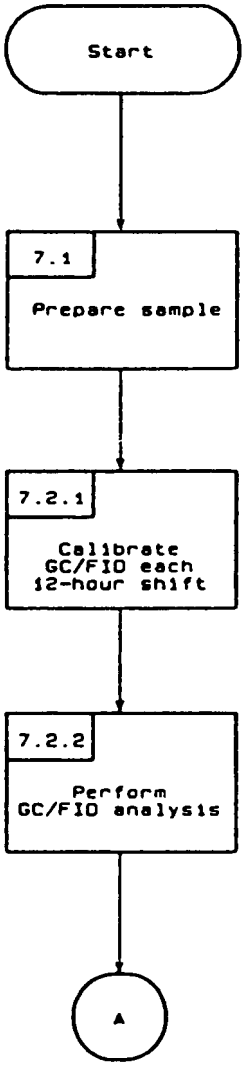
TABLE 2. QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH-LEVEL SOIL/SEDIMENTS

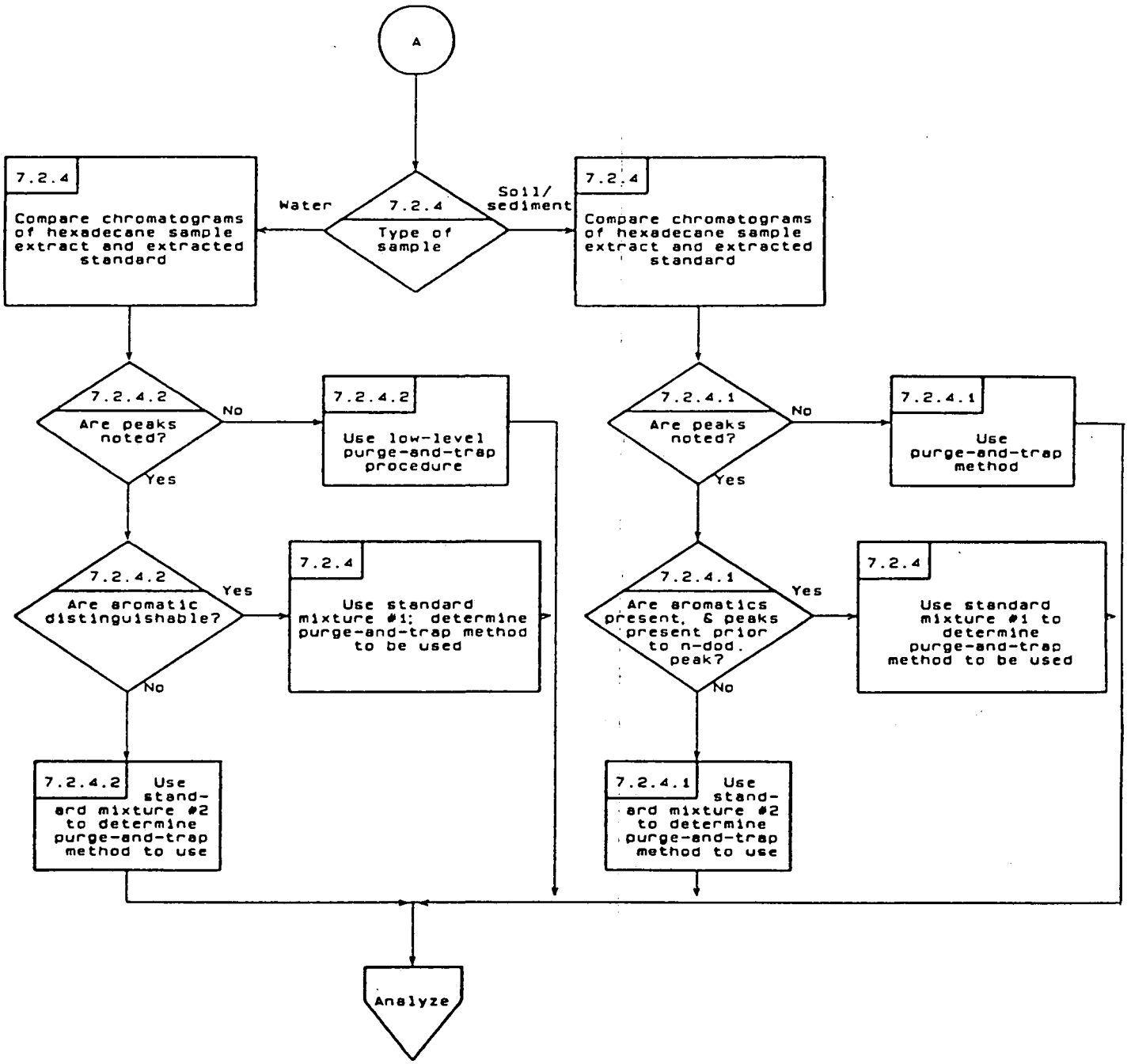
X Factor	Approximate Concentration Range [a]	Volume of Methanol Extract [b]
0.25-5.0	500-10,000 ug/kg	100 ul
0.5-10.0	1,000-20,000 ug/kg	50 ul
2.5-50.0	5,000-100,000 ug/kg	10 ul
12.5-250	25,000-500,000 ug/kg	100 uL of 1/50 dilution [c]

[a] Actual concentration ranges could be 10 to 20 times higher than this if the compounds are halogenated and the estimates are from GC/FID.

[b] The volume of methanol added to 5 mL of water being purged should be 100 uL. Therefore if the amount of methanol extract required is less than 100 uL, additional methanol should be added to maintain the constant 100-uL volume.

[c] Dilute an aliquot of the methanol extract and then take 100 uL for analysis.


Start
7.1
Prepare sample
7.2.1
Calibrate GC/FID each 12-hour shift
7.2.2
Perform GC/FID analysis
A


A
7.2.4
Type of sample
Water
Soil/ sediment
7.2.4
Compare chromatograms of hexadecane sample extract and extracted standard
7.2.4
Compare chromatograms of hexadecane sample extract and extracted standard
7.2.4.2
Are peaks noted?
No
Yes
7.2.4.2
Use low-level purge-and-trap procedure
7.2.4.2
Are aromatic distinguishable?
Yes
No
7.2.4
Use standard mixture #1; determine purge-and-trap method to be used
7.2.4.2
Use standard mixture #2 to determine purge-and-trap method to use
7.2.4.1
Are peaks noted?
No
Yes
7.2.4.1
Use purge-and-trap method
7.2.4.1
Are aromatics present, & peaks present prior to n-dod. peak?
Yes
No
7.2.4
Use standard mixture #1 to determine purge-and-trap method to be used
7.2.4.1
Use standard mixture #2 to determine purge-and-trap method to use
Analyze

APPENDIX

COMPANY REFERENCES

The following listing of frequently-used addresses is provided for the convenience of users of this manual. No endorsement is intended or implied.

Ace Glass Company
1342 N.W. Boulevard
P.O. Box 688
Vineland, NJ 08360
(609) 692-3333

Aldrich Chemical Company
Department T
P.O. Box 355
Milwaukee, WI 53201

Alpha Products
5570 - T W. 70th Place
Chicago, IL 60638
(312) 586-9810

Barneby and Cheney Company
E. 8th Avenue and N. Cassidy Street
P.O. Box 2526
Columbus, OH 43219
(614) 258-9501

Bio - Rad Laboratories
2200 Wright Avenue
Richmond, CA 94804
(415) 234-4130

Burdick & Jackson Lab Inc.
1953 S. Harvey Street
Muskegon, MO 49442

Calgon Corporation
P.O. Box 717
Pittsburgh, PA 15230
(412) 777-8000

Conostan Division
Conoco Speciality Products, Inc.
P.O. Box 1267
Ponca City, OK 74601
(405) 767-3456

Corning Glass Works
Houghton Park
Corning, NY 14830
(315) 974-9000

Dohrmann, Division of Xertex Corporation
3240 - T Scott Boulevard
Santa Clara, CA 95050
(408) 727-6000
(800) 538-7708

E. M. Laboratories, Inc.
500 Executive Boulevard
Elmsford, NY 10523

Fisher Scientific Co.
203 Fisher Building
Pittsburgh, PA 15219
(412) 562-8300

General Electric Corporation
3135 Easton Turnpike
Fairfield, CT 06431
(203) 373-2211

Graham Manufactory Co., Inc.
20 Florence Avenue
Batavia, NY 14020
(716) 343-2216

Hamilton Industries
1316 18th Street
Two Rivers, WI 54241
(414) 793-1121

ICN Life Sciences Group
3300 Hyland Avenue
Costa Mesa, CA 92626

Johns - Manville Corporation
P.O. Box 5108
Denver, CO 80217

Kontes Glass Company
8000 Spruce Street
Vineland, NJ 08360

Millipore Corporation
80 Ashby Road
Bedford, MA 01730
(617) 275-9200
(800) 225-1380

National Bureau of Standards
U.S. Department of Commerce
Washington, DC 20234
(202) 921-1000

Pierce Chemical Company
Box 117
Rockford, IL 61105
(815) 968-0747

Scientific Glass and Instrument, Inc.
7246 - T Wynnwood
P.O. Box 6
Houston, TX 77001
(713) 868-1481

Scientific Products Company
1430 Waukegon Road
McGaw Park, IL 60085
(312) 689-8410

Spex Industries
3880 - T and Park Avenue
Edison, NJ 08820

Waters Associates
34 - T Maple Street
Milford, MA 01757
(617) 478-2000
(800) 252-4752

Whatman Laboratory Products, Inc.
Clifton, NJ 07015
(201) 773-5800

Revision 0
Date September 1986

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United States
Environmental Protection
Agency

Office of Solid Waste
and Emergency Response
Washington, DC 20460

November 1986
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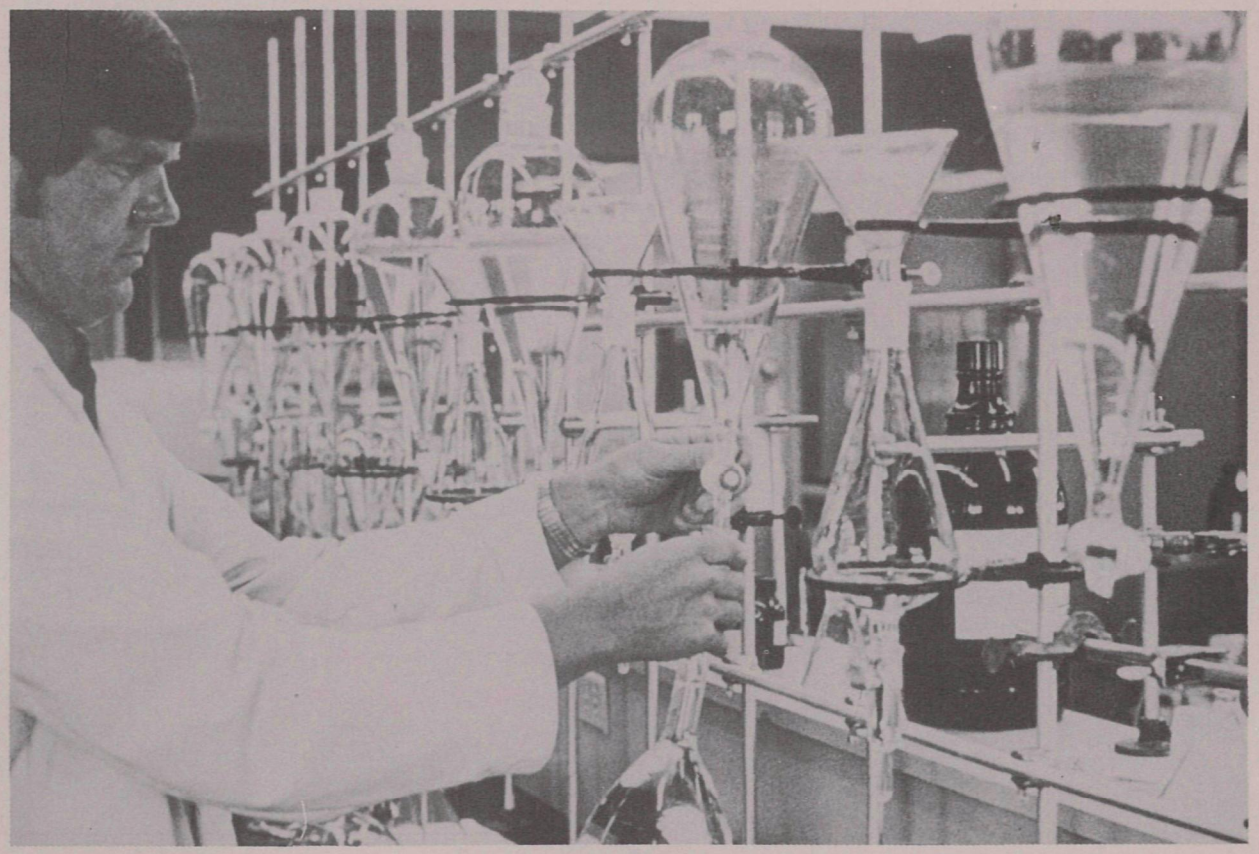
Solid Waste

EPA

Test Methods for Evaluating Solid Waste

Volume IC: Laboratory Manual Physical/Chemical Methods



METHOD STATUS TABLE
SW-846, THIRD EDITION, UPDATES I, II, AND IIA

September 1994

- Use this table as a reference guide to identify the promulgation status of SW-846 methods.
- The methods in this table are listed sequentially by number.
- This table should not be used as a Table of Contents for SW-846. Refer to the Table of Contents found in Final Update II (dated September 1994) for the order in which the methods appear in SW-846.

TABLE OF CONTENTS

VOLUME ONE

SECTION A

NOTE: A suffix of "A" in the method number indicates revision one (the method has been revised once). A suffix of "B" in the method number indicates revision two (the method has been revised twice). **In order to properly document the method used for analysis, the entire method number including the suffix letter designation (e.g., A or B) must be identified by the analyst.** A method reference found within the RCRA regulations and the text of SW-846 methods and chapters refers to the latest promulgated revision of the method, even though the method number does not include the appropriate letter suffix.

VOLUME ONE

SECTION B

NOTE: A suffix of "A" in the method number indicates revision one (the method has been revised once). A suffix of "B" in the method number indicates revision two (the method has been revised twice). **In order to properly document the method used for analysis, the entire method number including the suffix letter designation (e.g., A or B) must be identified by the analyst.** A method reference found within the RCRA regulations and the text of SW-846 methods and chapters refers to the latest promulgated revision of the method, even though the method number does not include the appropriate letter suffix.

VOLUME ONE

SECTION C

NOTE: A suffix of "A" in the method number indicates revision one (the method has been revised once). A suffix of "B" in the method number indicates revision two (the method has been revised twice). **In order to properly document the method used for analysis, the entire method number including the suffix letter designation (e.g., A or B) must be identified by the analyst.** A method reference found within the RCRA regulations and the text of SW-846 methods and chapters refers to the latest promulgated revision of the method, even though the method number does not include the appropriate letter suffix.

VOLUME TWO

NOTE: A suffix of "A" in the method number indicates revision one (the method has been revised once). A suffix of "B" in the method number indicates revision two (the method has been revised twice). **In order to properly document the method used for analysis, the entire method number including the suffix letter designation (e.g., A or B) must be identified by the analyst.** A method reference found within the RCRA regulations and the text of SW-846 methods and chapters refers to the latest promulgated revision of the method, even though the method number does not include the appropriate letter suffix.

SW-846 METHOD STATUS TABLE
September 1994

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
0010	--	--	Modified Method 5 Sampling Train	Vol II Chap 10	0010 Rev 0 9/86
0020	--	--	Source Assessment Sampling System (SASS)	Vol II Chap 10	0020 Rev 0 9/86
0030	--	--	Volatile Organic Sampling Train	Vol II Chap 10	0030 Rev 0 9/86
1010	--	--	Pensky-Martens Closed-Cup Method for Determining Ignitability	Vol IC Chap 8 Sec 8.1	1010 Rev 0 9/86
1020	1020A	--	Setaflash Closed-Cup Method for Determining Ignitability	Vol IC Chap 8 Sec 8.1	1020A Rev 1 7/92
1110	--	--	Corrosivity Toward Steel	Vol IC Chap 8 Sec 8.2	1110 Rev 0 9/86
1310	1310A	--	Extraction Procedure (EP) Toxicity Test Method and Structural Integrity Test	Vol IC Chap 8 Sec 8.4	1310A Rev 1 7/92
--	1311	--	Toxicity Characteristic Leaching Procedure	Vol IC Chap 8 Sec 8.4	1311 Rev 0 7/92
--	--	1312	Synthetic Precipitation Leaching Procedure	Vol IC Chap 6	1312 Rev 0 9/94

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
1320	--	--	Multiple Extraction Procedure	Vol IC Chap 6	1320 Rev 0 9/86
1330	1330A	--	Extraction Procedure for Oily Wastes	Vol IC Chap 6	1330A Rev 1 7/92
3005	3005A	--	Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy	Vol IA Chap 3 Sec 3.2	3005A Rev 1 7/92
3010	3010A	--	Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy	Vol IA Chap 3 Sec 3.2	3010A Rev 1 7/92
--	--	3015	Microwave Assisted Acid Digestion of Aqueous Samples and Extracts	Vol IA Chap 3 Sec 3.2	3015 Rev 0 9/94
3020	3020A	--	Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy	Vol IA Chap 3 Sec 3.2	3020A Rev 1 7/92
3040	--	--	Dissolution Procedure for Oils, Greases, or Waxes	Vol IA Chap 3 Sec 3.2	3040 Rev 0 9/86
3050	3050A	--	Acid Digestion of Sediments, Sludges, and Soils	Vol IA Chap 3 Sec 3.2	3050A Rev 1 7/92

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	--	3051	Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils	Vol IA Chap 3 Sec 3.2	3051 Rev 0 9/94
3500	3500A	--	Organic Extraction and Sample Preparation	Vol IB Chap 4 Sec 4.2.1	3500A Rev 1 7/92
3510	3510A	3510B	Separatory Funnel Liquid-Liquid Extraction	Vol IB Chap 4 Sec 4.2.1	3510B Rev 2 9/94
3520	3520A	3520B	Continuous Liquid-Liquid Extraction	Vol IB Chap 4 Sec 4.2.1	3520B Rev 2 9/94
3540	3540A	3540B	Soxhlet Extraction	Vol IB Chap 4 Sec 4.2.1	3540B Rev 2 9/94
--	--	3541	Automated Soxhlet Extraction	Vol IB Chap 4 Sec 4.2.1	3541 Rev 0 9/94
3550	--	3550A	Ultrasonic Extraction	Vol IB Chap 4 Sec 4.2.1	3550A Rev 1 9/94
3580	3580A	--	Waste Dilution	Vol IB Chap 4 Sec 4.2.1	3580A Rev 1 7/92
3600	3600A	3600B	Cleanup	Vol IB Chap 4 Sec 4.2.2	3600B Rev 2 9/94

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
3610	3610A	--	Alumina Column Cleanup	Vol IB Chap 4 Sec 4.2.2	3610A Rev 1 7/92
3611	3611A	--	Alumina Column Cleanup and Separation of Petroleum Wastes	Vol IB Chap 4 Sec 4.2.2	3611A Rev 1 7/92
3620	3620A	--	Florisil Column Cleanup	Vol IB Chap 4 Sec 4.2.2	3620A Rev 1 7/92
3630	3630A	3630B	Silica Gel Cleanup	Vol IB Chap 4 Sec 4.2.2	3630B Rev 2 9/94
3640	--	3640A	Gel-Permeation Cleanup	Vol IB Chap 4 Sec 4.2.2	3640A Rev 1 9/94
3650	3650A	--	Acid-Base Partition Cleanup	Vol IB Chap 4 Sec 4.2.2	3650A Rev 1 7/92
3660	3660A	--	Sulfur Cleanup	Vol IB Chap 4 Sec 4.2.2	3660A Rev 1 7/92
--	--	3665	Sulfuric Acid/Permanganate Cleanup	Vol IB Chap 4 Sec 4.2.2	3665 Rev 0 9/94
3810	--	--	Headspace	Vol IB Chap 4 Sec 4.4	3810 Rev 0 9/86

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
3820	--	--	Hexadecane Extraction and Screening of Purgeable Organics	Vol IB Chap 4 Sec 4.4	3820 Rev 0 9/86
--	--	4010 (Update IIA, dated 8/93)	Screening for Pentachlorophenol by Immunoassay	Vol IB Chap 4 Sec 4.4	4010 Rev 0 8/93
5030	5030A	--	Purge-and-Trap	Vol IB Chap 4 Sec 4.2.1	5030A Rev 1 7/92
5040	--	5040A	Analysis of Sorbent Cartridges from Volatile Organic Sampling Train (VOST): Gas Chromatography/Mass Spectrometry Technique	Vol IB Chap 4 Sec 4.2.1	5040A Rev 1 9/94
--	--	5041	Protocol for Analysis of Sorbent Cartridges from Volatile Organic Sampling Train (VOST): Wide-bore Capillary Column Technique	Vol IB Chap 4 Sec 4.2.1	5041 Rev 0 9/94
--	--	5050	Bomb Preparation Method for Solid Waste	Vol IC Chap 5	5050 Rev 0 9/94
6010	6010A	--	Inductively Coupled Plasma-Atomic Emission Spectroscopy	Vol IA Chap 3 Sec 3.3	6010A Rev 1 7/92

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	--	6020	Inductively Coupled Plasma - Mass Spectrometry	Vol IA Chap 3 Sec 3.3	6020 Rev 0 9/94
7000	7000A	--	Atomic Absorption Methods	Vol IA Chap 3 Sec 3.3	7000A Rev 1 7/92
7020	--	--	Aluminum (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7020 Rev 0 9/86
7040	--	--	Antimony (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7040 Rev 0 9/86
7041	--	--	Antimony (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7041 Rev 0 9/86
7060	--	7060A	Arsenic (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7060A Rev 1 9/94
7061	7061A	--	Arsenic (Atomic Absorption, Gaseous Hydride)	Vol IA Chap 3 Sec 3.3	7061A Rev 1 7/92
--	--	7062	Antimony and Arsenic (Atomic Absorption, Borohydride Reduction)	Vol IA Chap 3 Sec 3.3	7062 Rev 0 9/94
7080	--	7080A	Barium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7080A Rev 1 9/94

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	7081	--	Barium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7081 Rev 0 7/92
7090	--	--	Beryllium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7090 Rev 0 9/86
7091	--	--	Beryllium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7091 Rev 0 9/86
7130	--	--	Cadmium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7130 Rev 0 9/86
7131	--	7131A	Cadmium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7131A Rev I 9/94
7140	--	--	Calcium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7140 Rev 0 9/86
7190	--	--	Chromium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7190 Rev 0 9/86
7191	--	--	Chromium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7191 Rev 0 9/86
7195	--	--	Chromium, Hexavalent (Coprecipitation)	Vol IA Chap 3 Sec 3.3	7195 Rev 0 9/86

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
7196	7196A	--	Chromium, Hexavalent (Colorimetric)	Vol IA Chap 3 Sec 3.3	7196A Rev 1 7/92
7197	--	--	Chromium, Hexavalent (Chelation/Extrac-tion)	Vol IA Chap 3 Sec 3.3	7197 Rev 0 9/86
7198	--	--	Chromium, Hexavalent (Differential Pulse Polarography)	Vol IA Chap 3 Sec 3.3	7198 Rev 0 9/86
7200	--	--	Cobalt (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7200 Rev 0 9/86
7201	--	--	Cobalt (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7201 Rev 0 9/86
7210	--	--	Copper (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7210 Rev 0 9/86
--	7211	--	Copper (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7211 Rev 0 7/92
7380	--	--	Iron (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7380 Rev 0 9/86
--	7381	--	Iron (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7381 Rev 0 7/92

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
7420	--	--	Lead (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7420 Rev 0 9/86
7421	--	--	Lead (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7421 Rev 0 9/86
--	7430	--	Lithium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7430 Rev 0 7/92
7450	--	--	Magnesium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7450 Rev 0 9/86
7460	--	--	Manganese (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7460 Rev 0 9/86
--	7461	--	Manganese (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7461 Rev 0 7/92
7470	--	7470A	Mercury in Liquid Waste (Manual Cold-Vapor Technique)	Vol IA Chap 3 Sec 3.3	7470A Rev 1 9/94
7471	--	7471A	Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)	Vol IA Chap 3 Sec 3.3	7471A Rev 1 9/94
7480	--	--	Molybdenum (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7480 Rev 0 9/86

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
7481	--	--	Molybdenum (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7481 Rev 0 9/86
7520	--	--	Nickel (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7520 Rev 0 9/86
7550	--	--	Osmium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7550 Rev 0 9/86
7610	--	--	Potassium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7610 Rev 0 9/86
7740	--	--	Selenium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7740 Rev 0 9/86
7741	--	7741A	Selenium (Atomic Absorption, Gaseous Hydride)	Vol IA Chap 3 Sec 3.3	7741A Rev 1 9/94
--	--	7742	Selenium (Atomic Absorption, Borohydride Reduction)	Vol IA Chap 3 Sec 3.3	7742 Rev 0 9/94
7760	7760A	--	Silver (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7760A Rev 1 7/92
--	7761	--	Silver (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7761 Rev 0 7/92

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
7770	--	--	Sodium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7770 Rev 0 9/86
--	7780	--	Strontium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7780 Rev 0 7/92
7840	--	--	Thallium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7840 Rev 0 9/86
7841	--	--	Thallium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7841 Rev 0 9/86
7870	--	--	Tin (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7870 Rev 0 9/86
7910	--	--	Vanadium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7910 Rev 0 9/86
7911	--	--	Vanadium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7911 Rev 0 9/86
7950	--	--	Zinc (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7950 Rev 0 9/86
--	7951	--	Zinc (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7951 Rev 0 7/92

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
8000	8000A	--	Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8000A Rev 1 7/92
8010	8010A	8010B	Halogenated Volatile Organics by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8010B Rev 2 9/94
--	8011	--	1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane by Microextraction and Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8011 Rev 0 7/92
8015	8015A	--	Nonhalogenated Volatile Organics by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8015A Rev 1 7/92
8020	--	8020A	Aromatic Volatile Organics by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8020A Rev 1 9/94
--	8021	8021A	Halogenated Volatiles by Gas Chromatography Using Photoionization and Electrolytic Conductivity Detectors in Series: Capillary Column Technique	Vol IB Chap 4 Sec 4.3.1	8021A Rev 1 9/94
8030	8030A	--	Acrolein and Acrylonitrile by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8030A Rev 1 7/92
--	--	8031	Acrylonitrile by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8031 Rev 0 9/94

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	--	8032	Acrylamide by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8032 Rev 0 9/94
8040	8040A	--	Phenols by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8040A Rev 1 7/92
8060	--	--	Phthalate Esters	Vol IB Chap 4 Sec 4.3.1	8060 Rev 0 9/86
--	--	8061	Phthalate Esters by Capillary Gas Chromatography with Electron Capture Detection (GC/ECD)	Vol IB Chap 4 Sec 4.3.1	8061 Rev 0 9/94
--	8070	--	Nitrosamines by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8070 Rev 0 7/92
8080	--	8080A	Organochlorine Pesticides and Polychlorinated Biphenyls by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8080A Rev 1 9/94
--	--	8081	Organochlorine Pesticides and PCBs as Aroclors by Gas Chromatography: Capillary Column Technique	Vol IB Chap 4 Sec 4.3.1	8081 Rev 0 9/94
8090	--	--	Nitroaromatics and Cyclic Ketones	Vol IB Chap 4 Sec 4.3.1	8090 Rev 0 9/86

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
8100	--	--	Polynuclear Aromatic Hydrocarbons	Vol IB Chap 4 Sec 4.3.1	8100 Rev 0 9/86
--	8110	--	Haloethers by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8110 Rev 0 7/92
8120	--	8120A	Chlorinated Hydrocarbons by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8120A Rev 1 9/94
--	--	8121	Chlorinated Hydrocarbons by Gas Chromatography: Capillary Column Technique	Vol IB Chap 4 Sec 4.3.1	8121 Rev 0 9/94
8140	--	--	Organophosphorus Pesticides	Vol IB Chap 4 Sec 4.3.1	8140 Rev 0 9/86
--	8141	8141A	Organophosphorus Compounds by Gas Chromatography: Capillary Column Technique	Vol IB Chap 4 Sec 4.3.1	8141A Rev 1 9/94
8150	8150A	8150B	Chlorinated Herbicides by Gas Chromatography	Vol IB Chap 4 Sec. 4.3.1	8150B Rev 2 9/94
--	--	8151	Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzyl-ation Derivati-zation: Capillary Column Technique	Vol IB Chap 4 Sec 4.3.1	8151 Rev 0 9/94

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
8240	8240A	8240B	Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)	Vol IB Chap 4 Sec 4.3.2	8240B Rev 2 9/94
8250	--	8250A	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)	Vol IB Chap 4 Sec 4.3.2	8250A Rev 1 9/94
--	8260	8260A	Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique	Vol IB Chap 4 Sec 4.3.2	8260A Rev 1 9/94
8270	8270A	8270B	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique	Vol IB Chap 4 Sec 4.3.2	8270B Rev 2 9/94
--	--	8275	Thermal Chromatography/Mass Spectrometry (TC/MS) for Screening Semivolatile Organic Compounds	Vol IB Chap 4 Sec 4.4	8275 Rev 0 9/94
8280	--	--	The Analysis of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans	Vol IB Chap 4 Sec 4.3.2	8280 Rev 0 9/86

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	--	8290	Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS)	Vol IB Chap 4 Sec 4.3.2	8290 Rev 0 9/94
8310	--	--	Polynuclear Aromatic Hydrocarbons	Vol IB Chap 4 Sec 4.3.3	8310 Rev 0 9/86
--	--	8315	Determination of Carbonyl Compounds by High Performance Liquid Chromatography (HPLC)	Vol IB Chap 4 Sec 4.3.3	8315 Rev 0 9/94
--	--	8316	Acrylamide, Acrylonitrile and Acrolein by High Performance Liquid Chromatography (HPLC)	Vol IB Chap 4 Sec 4.3.3	8316 Rev 0 9/94
--	--	8318	N-Methylcarbamates by High Performance Liquid Chroma-tography (HPLC)	Vol IB Chap 4 Sec 4.3.3	8318 Rev 0 9/94

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METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	--	8321	Solvent Extractable Non-Volatile Compounds by High Performance Liquid Chromatography/Thermospray/Mass Spectrometry (HPLC/TSP/MS) or Ultraviolet (UV) Detection	Vol IB Chap 4 Sec 4.3.3	8321 Rev 0 9/94
--	--	8330	Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)	Vol IB Chap 4 Sec 4.3.3	8330 Rev 0 9/94
--	--	8331	Tetrazene by Reverse Phase High Performance Liquid Chromatography (HPLC)	Vol IB Chap 4 Sec 4.3.3	8331 Rev 0 9/94
--	--	8410	Gas Chromatography/Fourier Transform Infrared (GC/FT-IR) Spectrometry for Semivolatile Organics: Capillary Column	Vol IB Chap 4 Sec 4.3.4	8410 Rev 0 9/94
9010	9010A	--	Total and Amenable Cyanide (Colorimetric, Manual)	Vol IC Chap 5	9010A Rev 1 7/92
9012	--	--	Total and Amenable Cyanide (Colorimetric, Automated UV)	Vol IC Chap 5	9012 Rev 0 9/86

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	9013	--	Cyanide Extraction Procedure for Solids and Oils	Vol IC Chap 5	9013 Rev 0 7/92
9020	9020A	9020B	Total Organic Halides (TOX)	Vol IC Chap 5	9020B Rev 2 9/94
--	9021	--	Purgeable Organic Halides (POX)	Vol IC Chap 5	9021 Rev 0 7/92
9022	--	--	Total Organic Halides (TOX) by Neutron Activation Analysis	Vol IC Chap 5	9022 Rev 0 9/86
9030	9030A	--	Acid-Soluble and Acid-Insoluble Sulfides	Vol IC Chap 5	9030A Rev 1 7/92
--	9031	--	Extractable Sulfides	Vol IC Chap 5	9031 Rev 0 7/92
9035	--	--	Sulfate (Colorimetric, Automated, Chloranilate)	Vol IC Chap 5	9035 Rev 0 9/86
9036	--	--	Sulfate (Colorimetric, Automated, Methylthymol Blue, AA II)	Vol IC Chap 5	9036 Rev 0 9/86
9038	--	--	Sulfate (Turbidimetric)	Vol IC Chap 5	9038 Rev 0 9/86

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METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
9040	--	9040A	pH Electrometric Measurement	Vol IC Chap 6	9040A Rev 1 9/94
9041	9041A	--	pH Paper Method	Vol IC Chap 6	9041A Rev 1 7/92
9045	9045A	9045B	Soil and Waste pH	Vol IC Chap 6	9045B Rev 2 9/94
9050	--	--	Specific Conductance	Vol IC Chap 6	9050 Rev 0 9/86
--	--	9056	Determination of Inorganic Anions by Ion Chromatography	Vol IC Chap 5	9056 Rev 0 9/94
9060	--	--	Total Organic Carbon	Vol IC Chap 5	9060 Rev 0 9/86
9065	--	--	Phenolics (Spectrophotometric, Manual 4-AAP with Distillation)	Vol IC Chap 5	9065 Rev 0 9/86
9066	--	--	Phenolics (Colorimetric, Automated 4-AAP with Distillation)	Vol IC Chap 5	9066 Rev 0 9/86
9067	--	--	Phenolics (Spectrophotometric, MBTH with Distillation)	Vol IC Chap 5	9067 Rev 0 9/86

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
9070	--	--	Total Recoverable Oil & Grease (Gravimetric, Separatory Funnel Extraction)	Vol IC Chap 5	9070 Rev 0 9/86
9071	--	9071A	Oil and Grease Extraction Method for Sludge and Sediment Samples	Vol IC Chap 5	9071A Rev 1 9/94
--	--	9075	Test Method for Total Chlorine in New and Used Petroleum Products by X-Ray Fluorescence Spectrometry (XRF)	Vol IC Chap 5	9075 Rev 0 9/94
--	--	9076	Test Method for Total Chlorine in New and Used Petroleum Products by Oxidative Combustion and Microcoulometry	Vol IC Chap 5	9076 Rev 0 9/94
--	--	9077	Test Methods for Total Chlorine in New and Used Petroleum Products (Field Test Kit Methods)	Vol IC Chap 5	9077 Rev 0 9/94
9080	--	--	Cation-Exchange Capacity of Soils (Ammonium Acetate)	Vol IC Chap 6	9080 Rev 0 9/86
9081	--	--	Cation-Exchange Capacity of Soils (Sodium Acetate)	Vol IC Chap 6	9081 Rev 0 9/86

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
9090	9090A	--	Compatibility Test for Wastes and Membrane Liners	Vol IC Chap 6	9090A Rev 1 7/92
9095	--	--	Paint Filter Liquids Test	Vol IC Chap 6	9095 Rev 0 9/86
--	--	9096	Liquid Release Test (LRT) Procedure	Vol IC Chap 6	9096 Rev 0 9/94
9100	--	--	Saturated Hydraulic Conductivity, Saturated Leachate Conductivity, and Intrinsic Permeability	Vol IC Chap 6	9100 Rev 0 9/86
9131	--	--	Total Coliform: Multiple Tube Fermentation Technique	Vol IC Chap 5	9131 Rev 0 9/86
9132	--	--	Total Coliform: Membrane Filter Technique	Vol IC Chap 5	9132 Rev 0 9/86
9200	--	--	Nitrate	Vol IC Chap 5	9200 Rev 0 9/86
9250	--	--	Chloride (Colorimetric, Automated Ferricyanide AAI)	Vol IC Chap 5	9250 Rev 0 9/86
9251	--	--	Chloride (Colorimetric, Automated Ferricyanide AAII)	Vol IC Chap 5	9251 Rev 0 9/86

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METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
9252	--	9252A	Chloride (Titrimetric, Mercuric Nitrate)	Vol IC Chap 5	9252A Rev 1 9/94
--	--	9253	Chloride (Titrimetric, Silver Nitrate)	Vol IC Chap 5	9253 Rev 0 9/94
9310	--	--	Gross Alpha and Gross Beta	Vol IC Chap 6	9310 Rev 0 9/86
9315	--	--	Alpha-Emitting Radium Isotopes	Vol IC Chap 6	9315 Rev 0 9/86
9320	--	--	Radium-228	Vol IC Chap 5	9320 Rev 0 9/86
HCN Test Method	HCN Test Method	HCN Test Method	Test Method to Determine Hydrogen Cyanide Released from Wastes	Vol IC Chap 7 Sec 7.3	Guidance Method Only
H_2S Test Method	H_2S Test Method	H_2S Test Method	Test Method to Determine Hydrogen Sulfide Released from Wastes	Vol IC Chap 7 Sec 7.3	Guidance Method Only

DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency.

SW-846 methods are designed to be used with equipment from any manufacturer that results in suitable method performance (as assessed by accuracy, precision, detection limits and matrix compatibility). In several SW-846 methods, equipment specifications and settings are given for the specific instrument used during method development, or subsequently approved for use in the method. These references are made to provide the best possible guidance to laboratories using this manual. Equipment not specified in the method may be used as long as the laboratory achieves equivalent or superior method performance. If alternate equipment is used, the laboratory must follow the manufacturer's instructions for their particular instrument.

Since many types and sizes of glassware and supplies are commercially available, and since it is possible to prepare reagents and standards in many different ways, those specified in these methods may be replaced by any similar types as long as this substitution does not affect the overall quality of the analyses.

ABSTRACT

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846) provides test procedures and guidance which are recommended for use in conducting the evaluations and measurements needed to comply with the Resource Conservation and Recovery Act (RCRA), Public Law 94-580, as amended. These methods are approved by the U.S. Environmental Protection Agency for obtaining data to satisfy the requirements of 40 CFR Parts 122 through 270 promulgated under RCRA, as amended. This manual presents the state-of-the-art in routine analytical tested adapted for the RCRA program. It contains procedures for field and laboratory quality control, sampling, determining hazardous constituents in wastes, determining the hazardous characteristics of wastes (toxicity, ignitability, reactivity, and corrosivity), and for determining physical properties of wastes. It also contains guidance on how to select appropriate methods.

Several of the hazardous waste regulations under Subtitle C of RCRA require that specific testing methods described in SW-846 be employed for certain applications. Refer to 40 *Code of Federal Regulations* (CFR), Parts 260 through 270, for those specific requirements. Any reliable analytical method may be used to meet other requirements under Subtitle C of RCRA.

METHOD INDEX AND CONVERSION TABLE

Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
0010	Ten	0010	0
0020	Ten	0020	0
0030	Ten	0030	0
1010	Eight (8.1)	1010	0
1020	Eight (8.1)	1020	0
1110	Eight (8.2)	1110	0
1310	Eight (8.4)	1310	0
1320	Six	1320	0
1330	Six	1330	0
3005	Three	3005	0
3010	Three	3010	0
3020	Three	3020	0
3040	Three	3040	0
3050	Three	3050	0
3500	Four (4.2.1)	None (new method)	0
3510	Four (4.2.1)	3510	0
3520	Four (4.2.1)	3520	0
3540	Four (4.2.1)	3540	0
3550	Four (4.2.1)	3550	0
3580	Four (4.2.1)	None (new method)	0
3600	Four (4.2.2)	None (new method)	0
3610	Four (4.2.2)	None (new method)	0
3611	Four (4.2.2)	3570	0
3620	Four (4.2.2)	None (new method)	0
3630	Four (4.2.2)	None (new method)	0
3640	Four (4.2.2)	None (new method)	0
3650	Four (4.2.2)	None (new method)	0
3660	Four (4.2.2)	None (new method)	0
3810	Four (4.4)	5020	0
3820	Four (4.4)	None (new method)	0
5030	Four (4.2.1)	5030	0
5040	Four (4.2.1)	3720	0
6010	Three	6010	0
7000	Three	7000	0
7020	Three	7020	0

Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
7040	Three	7040	0
7041	Three	7041	0
7060	Three	7060	0
7061	Three	7061	0
7080	Three	7080	0
7090	Three	7090	0
7091	Three	7091	0
7130	Three	7130	0
7131	Three	7131	0
7140	Three	7140	0
7190	Tnree	7190	0
7191	Three	7191	0
7195	Three	7195	0
7196	Three	7196	0
7197	Three	7197	0
7198	Three	7198	0
7200	Three	7200	0
7201	Three	7201	0
7210	Three	7210	0
7380	Three	7380	0
7420	Three	7420	0
7421	Three	7421	0
7450	Three	7450	0
7460	Three	7460	0
7470	Three	7470	0
7471	Three	7471	0
7480	Three	7480	0
7481	Three	7481	0
7520	Three	7520	0
7550	Three	7550	0
7610	Three	7610	0
7740	Three	7740	0
7741	Three	7741	0
7760	Three	7760	0
7770	Three	7770	0

Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
7840	Three	7840	0
7841	Three	7841	0
7870	Three	7870	0
7910	Three	7910	0
7911	Three	7911	0
7950	Three	7950	0
8000	Four (4.3.1)	None (new method)	0
8010	Four (4.3.1)	8010	0
8015	Four (4.3.1)	8015	0
8020	Four (4.3.1)	8020	0
8030	Four (4.3.1)	8030	0
8040	Four (4.3.1)	8040	0
8060	Four (4.3.1)	8060	0
8080	Four (4.3.1)	8080	0
8090	Four (4.3.1)	8090	0
8100	Four (4.3.1)	8100	0
8120	Four (4.3.1)	8120	0
8140	Four (4.3.1)	8140	0
8150	Four (4.3.1)	8150	0
8240	Four (4.3.2)	8240	0
8250	Four (4.3.2)	8250	0
8270	Four (4.3.2)	8270	0
8280	Four (4.3.2)	None (new method)	0
8310	Four (4.3.3)	8310	0
9010	Five	9010	0
9020	Five	9020	0
9022	Five	9022	0
9030	Five	9030	0
9035	Five	9035	0
9036	Five	9036	0
9038	Five	9038	0
9040	Six	9040	0
9041	Six	9041	0
9045	Six	9045	0
9050	Six	9050	0

METHOD INDEX AND CONVERSION TABLE
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Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
9060	Five	9060	0
9065	Five	9065	0
9066	Five	9066	0
9067	Five	9067	0
9070	Five	9070	0
9071	Five	9071	0
9080	Six	9080	0
9081	Six	9081	0
9090	Six	9090	0
9095	Six	9095	0
9100	Six	9100	0
9131	Five	9131	0
9132	Five	9132	0
9200	Five	9200	0
9250	Five	9250	0
9251	Five	9251	0
9252	Five	9252	0
9310	Six	9310	0
9315	Six	9315	0
9320	Five	9320	0
HCN Test Method	Seven	HCN Test Method	0
H_2S Test Method	Seven	H_2S Test Method	0

PURPOSE OF THE MANUAL

Test Methods for Evaluating Solid Waste (SW-846) is intended to provide a unified, up-to-date source of information on sampling and analysis related to compliance with RCRA regulations. It brings together into one reference all sampling and testing methodology approved by the Office of Solid Waste for use in implementing the RCRA regulatory program. The manual provides methodology for collecting and testing representative samples of waste and other materials to be monitored. Aspects of sampling and testing covered in SW-846 include quality control, sampling plan development and implementation, analysis of inorganic and organic constituents, the estimation of intrinsic physical properties, and the appraisal of waste characteristics.

The procedures described in this manual are meant to be comprehensive and detailed, coupled with the realization that the problems encountered in sampling and analytical situations require a certain amount of flexibility. The solutions to these problems will depend, in part, on the skill, training, and experience of the analyst. For some situations, it is possible to use this manual in rote fashion. In other situations, it will require a combination of technical abilities, using the manual as guidance rather than in a step-by-step, word-by-word fashion. Although this puts an extra burden on the user, it is unavoidable because of the variety of sampling and analytical conditions found with hazardous wastes.

ORGANIZATION AND FORMAT

This manual is divided into two volumes. Volume I focuses on laboratory activities and is divided for convenience into three sections. Volume IA deals with quality control, selection of appropriate test methods, and analytical methods for metallic species. Volume IB consists of methods for organic analytes. Volume IC includes a variety of test methods for miscellaneous analytes and properties for use in evaluating the waste characteristics. Volume II deals with sample acquisition and includes quality control, sampling plan design and implementation, and field sampling methods. Included for the convenience of sampling personnel are discusssions of the ground water, land treatment, and incineration monitoring regulations.

Volume I begins with an overview of the quality control precedures to be imposed upon the sampling and analytical methods. The quality control chapter (Chapter One) and the methods chapters are interdependent. The analytical procedures cannot be used without a thorough understanding of the quality control requirements and the means to implement them. This understanding can be achieved only be reviewing Chapter One and the analytical methods together. It is expected that individual laboratories, using SW-846 as the reference

source, will select appropriate methods and develop a standard operating procedure (SOP) to be followed by the laboratory. The SOP should incorporate the pertinent information from this manual adopted to the specific needs and circumstances of the individual laboratory as well as to the materials to be evaluated.

The method selection chapter (Chapter Two) presents a comprehensive discussion of the application of these methods to various matrices in the determination of groups of analytes or specific analytes. It aids the chemist in constructing the correct analytical method from the array of procedures which may cover the matrix/analyte/concentration combination of interests. The section discusses the objective of the testing program and its relationship to the choice of an analytical method. Flow charts are presented along with tables to guide in the selection of the correct analytical procedures to form the appropriate method.

The analytical methods are separated into distinct procedures describing specific, independent analytical operations. These include extraction, digestion, cleanup, and determination. This format allows linking of the various steps in the analysis according to: the type of sample (e.g., water, soil, sludge, still bottom); analytes(s) of interest; needed sensitivity; and available analytical instrumentation. The chapters describing Miscellaneous Test Methods and Properties, however, give complete methods which are not amenable to such segmentation to form discrete procedures.

The introductory material at the beginning of each section containing analytical procedures presents information on sample handling and preservation, safety, and sample preparation.

Part II of Volume I (Chapters Seven and Eight) describes the characteristics of a waste. Sections following the regulatory descriptions contain the methods used to determine if the waste is hazardous because it exhibits a particular characteristic.

Volume II gives background information on statistical and nonstatistical aspects of sampling. It also presents practical sampling techniques appropriate for situations presenting a variety of physical conditions.

A discussion of the regulatory requirements with respect to several monitoring categories is also given in this volume. These include ground water monitoring, land treatment, and incineration. The purpose of this guidance is to orient the user to the objective of the analysis, and to assist in developing data quality objectives, sampling plans, and laboratory SOP's.

Significant interferences, or other problems, may be encountered with certain samples. In these situations, the analyst is advised to contact the Chief, Methods Section (WH-562B) Technical Assessment Branch, Office of Solid Waste, US EPA, Washington, DC 20460 (202-382-4761) for assistance. The manual is intended to serve all those with a need to evaluate solid waste. Your comments, corrections, suggestions, and questions concerning any material contained in, or omitted from, this manual will be gratefully appreciated. Please direct your comments to the above address.

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CHAPTER ONE
QUALITY CONTROL

1.0 INTRODUCTION

It is the goal of the U.S. Environmental Protection Agency's (EPA's) quality assurance (QA) program to ensure that all data be scientifically valid, defensible, and of known precision and accuracy. The data should be of sufficient known quality to withstand scientific and legal challenge relative to the use for which the data are obtained. The QA program is management's tool for achieving this goal.

For RCRA analyses, the recommended minimum requirements for a QA program and the associated quality control (QC) procedures are provided in this chapter.

The data acquired from QC procedures are used to estimate the quality of analytical data, to determine the need for corrective action in response to identified deficiencies, and to interpret results after corrective action procedures are implemented. Method-specific QC procedures are incorporated in the individual methods since they are not applied universally.

A total program to generate data of acceptable quality should include both a QA component, which encompasses the management procedures and controls, as well as an operational day-to-day QC component. This chapter defines fundamental elements of such a data collection program. Data collection efforts involve:

1. design of a project plan to achieve the data quality objectives (DQOs);

2. implementation of the project plan; and

3. assessment of the data to determine if the DQOs are met.

The project plan may be a sampling and analysis plan or a waste analysis plan if it covers the QA/QC goals of the Chapter, or it may be a Quality Assurance Project Plan as described later in this chapter.

This chapter identifies the minimal QC components that should be used in the performance of sampling and analyses, including the QC information which should be documented. Guidance is provided to construct QA programs for field and laboratory work conducted in support of the RCRA program.

2.0 QA PROJECT PLAN

It is recommended that all projects which generate environment-related data in support of RCRA have a QA Project Plan (QAPjP) or equivalent. In some instances, a sampling and analysis plan or a waste analysis plan may be equivalent if it covers all of the QA/QC goals outlined in this chapter. In addition, a separate QAPjP need not be prepared for routine analyses or activities where the procedures to be followed are described in a Standard

Operating Procedures manual or similar document and include the elements of a QAPjP. These documents should be available and referenced in the documentation and/or records for the analysis activities. The term "QAPjP" in this chapter refers to any of these QA/QC documents.

The QAPjP should detail the QA/QC goals and protocols for a specific data collection activity. The QAPjP sets forth a plan for sampling and analysis activities that will generate data of a quality commensurate with their intended use. QAPjP elements should include a description of the project and its objectives; a statement of the DQOs of the project; identification of those involved in the data collection and their responsibilities and authorities; reference to (or inclusion of) the specific sample collection and analysis procedures that will be followed for all aspects of the project; enumeration of QC procedures to be followed; and descriptions of all project documentation. Additional elements should be included in the QAPjP if needed to address all quality related aspects of the data collection project. Elements should be omitted only when they are inappropriate for the project or when absence of those elements will not affect the quality of data obtained for the project (see reference 1).

The role and importance of DQOs and project documentation are discussed below in Sections 2.1 through 2.6. Management and organization play a critical role in determining the effectiveness of a QA/QC program and ensuring that all required procedures are followed. Section 2.7 discusses the elements of an organization's QA program that have been found to ensure an effective program. Field operations and laboratory operations (along with applicable QC procedures) are discussed in Sections 3 and 4, respectively.

2.1 DATA QUALITY OBJECTIVES

Data quality objectives (DQOs) for the data collection activity describe the overall level of uncertainty that a decision-maker is willing to accept in results derived from environmental data. This uncertainty is used to specify the quality of the measurement data required, usually in terms of objectives for precision, bias, representativeness, comparability and completeness. The DQOs should be defined prior to the initiation of the field and laboratory work. The field and laboratory organizations performing the work should be aware of the DQOs so that their personnel may make informed decisions during the course of the project to attain those DQOs. More detailed information on DQOs is available from the U.S. EPA Quality Assurance Management Staff (QAMS) (see references 2 and 4).

2.2 PROJECT OBJECTIVES

A statement of the project objectives and how the objectives are to be attained should be concisely stated and sufficiently detailed to permit clear understanding by all parties involved in the data collection effort. This includes a statement of what problem is to be solved and the information required

in the process. It also includes appropriate statements of the DQOs (i.e., the acceptable level of uncertainty in the information).

2.3 SAMPLE COLLECTION

Sampling procedures, locations, equipment, and sample preservation and handling requirements should be specified in the QAPjP. Further details on quality assurance procedures for field operations are described in Section 3 of this chapter. The OSW is developing policies and procedures for sampling in a planned revision of Chapter Nine of this manual. Specific procedures for groundwater sampling are provided in Chapter Eleven of this manual.

2.4 ANALYSIS AND TESTING

Analytes and properties of concern, analytical and testing procedures to be employed, required detection limits, and requirements for precision and bias should be specified. All applicable regulatory requirements and the project DQOs should be considered when developing the specifications. Further details on the procedures for analytical operations are described in Section 4 of this chapter.

2.5 QUALITY CONTROL

The quality assurance program should address both field and laboratory activities. Quality control procedures should be specified for estimating the precision and bias of the data. Recommended minimum requirements for QC samples have been established by EPA and should be met in order to satisfy recommended minimum criteria for acceptable data quality. Further details on procedures for field and laboratory operations are described in Sections 3 and 4, respectively, of this chapter.

2.6 PROJECT DOCUMENTATION

Documents should be prepared and maintained in conjunction with the data collection effort. Project documentation should be sufficient to allow review of all aspects of the work being performed. The QAPjP discussed in Sections 3 and 4 is one important document that should be maintained.

The length of storage time for project records should comply with regulatory requirements, organizational policy, or project requirements, whichever is more stringent. It is recommended that documentation be stored for three years from submission of the project final report.

Documentation should be secured in a facility that adequately addresses/minimizes its deterioration for the length of time that it is to be retained. A system allowing for the expedient retrieval of information should exist.

Access to archived information should be controlled to maintain the integrity of the data. Procedures should be developed to identify those individuals with access to the data.

2.7 ORGANIZATION PERFORMING FIELD OR LABORATORY OPERATIONS

Proper design and structure of the organization facilitates effective and efficient transfer of information and helps to prevent important procedures from being overlooked.

The organizational structure, functional responsibilities, levels of authority, job descriptions, and lines of communication for all project activities should be established and documented. One person may cover more than one organizational function. Each project participant should have a clear understanding of his or her duties and responsibilities and the relationship of those responsibilities to the overall data collection effort.

The management of each organization participating in a project involving data collection activities should establish that organization's operational and QA policies. This information should be documented in the QAPjP. The management should ensure that (1) the appropriate methodologies are followed as documented in the QAPjPs; (2) personnel clearly understand their duties and responsibilities; (3) each staff member has access to appropriate project documents; (4) any deviations from the QAPjP are communicated to the project management and documented; and (5) communication occurs between the field, laboratory, and project management, as specified in the QAPjP. In addition, each organization should ensure that their activities do not increase the risk to humans or the environment at or about the project location. Certain projects may require specific policies or a Health and Safety Plan to provide this assurance.

The management of the participating field or laboratory organization should establish personnel qualifications and training requirements for the project. Each person participating in the project should have the education, training, technical knowledge, and experience, or a combination thereof, to enable that individual to perform assigned functions. Training should be provided for each staff member as necessary to perform their functions properly. Personnel qualifications should be documented in terms of education, experience, and training, and periodically reviewed to ensure adequacy to current responsibilities.

Each participating field organization or laboratory organization should have a designated QA function (i.e., a team or individual trained in QA) to monitor operations to ensure that the equipment, personnel, activities, procedures, and documentation conform with the QAPjP. To the extent possible, the QA monitoring function should be entirely separate from, and independent of, personnel engaged in the work being monitored. The QA function should be responsible for the QA review.

2.7.1 Performance Evaluation

Performance evaluation studies are used to measure the performance of the laboratory on unknown samples. Performance evaluation samples are typically submitted to the laboratory as blind samples by an independent outside source. The results are compared to predetermined acceptance limits. Performance evaluation samples can also be submitted to the laboratory as part of the QA function during internal assessment of laboratory performance. Records of all performance evaluation studies should be maintained by the laboratory. Problems identified through participation in performance evaluation studies should be immediately investigated and corrected.

2.7.2 Internal Assessment by QA Function

Personnel performing field and laboratory activities are responsible for continually monitoring individual compliance with the QAPjP. The QA function should review procedures, results and calculations to determine compliance with the QAPjP. The results of this internal assessment should be reported to management with requirements for a plan to correct observed deficiencies.

2.7.3 External Assessment

The field and laboratory activities may be reviewed by personnel external to the organization. Such an assessment is an extremely valuable method for identifying overlooked problems. The results of the external assessment should be submitted to management with requirements for a plan to correct observed deficiencies.

2.7.4 On-Site Evaluation

On-site evaluations may be conducted as part of both internal and external assessments. The focus of an on-site evaluation is to evaluate the degree of conformance of project activities with the applicable QAPjP. On-site evaluations may include, but are not limited to, a complete review of facilities, staff, training, instrumentation, procedures, methods, sample collection, analyses, QA policies and procedures related to the generation of environmental data. Records of each evaluation should include the date of the evaluation, location, the areas reviewed, the person performing the evaluation, findings and problems, and actions recommended and taken to resolve problems. Any problems identified that are likely to affect data integrity should be brought immediately to the attention of management.

2.7.4.1 Field Activities

The review of field activities should be conducted by one or more persons knowledgeable in the activities being reviewed and include evaluating, at a minimum, the following subjects:

Completeness of Field Reports -- This review determines whether all requirements for field activities in the QAPjP have been fulfilled, that complete records exist for each field activity, and that the procedures

specified in the QAPjP have been implemented. Emphasis on field documentation will help assure sample integrity and sufficient technical information to recreate each field event. The results of this completeness check should be documented, and environmental data affected by incomplete records should be identified.

Identification of Valid Samples -- This review involves interpretation and evaluation of the field records to detect problems affecting the representativeness of environmental samples. Examples of items that might indicate potentially invalid samples include improper well development, improperly screened wells, instability of pH or conductivity, and collection of volatiles near internal combustion engines. The field records should be evaluated against the QAPjP and SOPs. The reviewer should document the sample validity and identify the environmental data associated with any poor or incorrect field work.

Correlation of Field Test Data -- This review involves comparing any available results of field measurements obtained by more than one method. For example, surface geophysical methods should correlate with direct methods of site geologic characterization such as lithologic logs constructed during drilling operations.

Identification of Anomalous Field Test Data -- This review identifies any anomalous field test data. For example, a water temperature for one well that is 5 degrees higher than any other well temperature in the same aquifer should be noted. The reviewer should evaluate the impact of anomalous field measurement results on the associated environmental data.

Validation of Field Analyses -- This review validates and documents all data from field analysis that are generated in situ or from a mobile laboratory as specified in Section 2.7.4.2. The reviewer should document whether the QC checks meet the acceptance criteria, and whether corrective actions were taken for any analysis performed when acceptance criteria were exceeded.

2.7.4.2 Laboratory Activities

The review of laboratory data should be conducted by one or more persons knowledgeable in laboratory activities and include evaluating, at a minimum, the following subjects:

Completeness of Laboratory Records -- This review determines whether: (1) all samples and analyses required by the QAPjP have been processed, (2) complete records exist for each analysis and the associated QC samples, and that (3) the procedures specified in the QAPjP have been implemented. The results of the completeness check should be documented, and environmental data affected by incomplete records should be identified.

Evaluation of Data with Respect to Detection and Quantitation Limits -- This review compares analytical results to required quantitation limits. Reviewers should document instances where detection or quantitation limits

exceed regulatory limits, action levels, or target concentrations specified in the QAPjP.

Evaluation of Data with Respect to Control Limits -- This review compares the results of QC and calibration check samples to control criteria. Corrective action should be implemented for data not within control limits. The reviewer should check that corrective action reports, and the results of reanalysis, are available. The review should determine whether samples associated with out-of-control QC data are identified in a written record of the data review, and whether an assessment of the utility of such analytical results is recorded.

Review of Holding Time Data -- This review compares sample holding times to those required by the QAPjP, and notes all deviations.

Review of Performance Evaluation (PE) Results -- PE study results can be helpful in evaluating the impact of out-of-control conditions. This review documents any recurring trends or problems evident in PE studies and evaluates their effect on environmental data.

Correlation of Laboratory Data -- This review determines whether the results of data obtained from related laboratory tests, e.g., Purgeable Organic Halides (POX) and Volatile Organics, are documented, and whether the significance of any differences is discussed in the reports.

2.7.5 QA Reports

There should be periodic reporting of pertinent QA/QC information to the project management to allow assessment of the overall effectiveness of the QA program. There are three major types of QA reports to project management:

Periodic Report on Key QA Activities -- Provides summary of key QA activities during the period, stressing measures that are being taken to improve data quality; describes significant quality problems observed and corrective actions taken; reports information regarding any changes in certification/accreditation status; describes involvement in resolution of quality issues with clients or agencies; reports any QA organizational changes; and provides notice of the distribution of revised documents controlled by the QA organization (i.e., procedures).

Report on Measurement Quality Indicators -- Includes the assessment of QC data gathered over the period, the frequency of analyses repeated due to unacceptable QC performance, and, if possible, the reason for the unacceptable performance and corrective action taken.

Reports on QA Assessments -- Includes the results of the assessments and the plan for correcting identified deficiencies; submitted immediately following any internal or external on-site evaluation or upon receipt of the results of any performance evaluation studies.

3.0 FIELD OPERATIONS

The field operations should be conducted in such a way as to provide reliable information that meets the DQOs. To achieve this, certain minimal policies and procedures should be implemented. The OSW is considering revisions of Chapter Nine and Eleven of this manual. Supplemental information and guidance is available in the RCRA Ground-Water Monitoring Technical Enforcement Guidance Document (TEGD) (Reference 3). The project documentation should contain the information specified below.

3.1 FIELD LOGISTICS

The QAPjP should describe the type(s) of field operations to be performed and the appropriate area(s) in which to perform the work. The QAPjP should address ventilation, protection from extreme weather and temperatures, access to stable power, and provision for water and gases of required purity.

Whenever practical, the sampling site facilities should be examined prior to the start of work to ensure that all required items are available. The actual area of sampling should be examined to ensure that trucks, drilling equipment, and personnel have adequate access to the site.

The determination as to whether sample shipping is necessary should be made during planning for the project. This need is established by evaluating the analyses to be performed, sample holding times, and location of the site and the laboratory. Shipping or transporting of samples to a laboratory should be done within a timeframe such that recommended holding times are met.

Samples should be packaged, labelled, preserved (e.g., preservative added, iced, etc.), and documented in an area which is free of contamination and provides for secure storage. The level of custody and whether sample storage is needed should be addressed in the QAPjP.

Storage areas for solvents, reagents, standards, and reference materials should be adequate to preserve their identity, concentration, purity, and stability prior to use.

Decontamination of sampling equipment may be performed at the location where sampling occurs, prior to going to the sampling site, or in designated areas near the sampling site. Project documentation should specify where and how this work is accomplished. If decontamination is to be done at the site, water and solvents of appropriate purity should be available. The method of accomplishing decontamination, including the required materials, solvents, and water purity should be specified.

During the sampling process and during on-site or <u>in situ</u> analyses, waste materials are sometimes generated. The method for storage and disposal of these waste materials that complies with applicable local, state and Federal regulations should be specified. Adequate facilities should be provided for the collection and storage of all wastes, and these facilities should be operated so

as to minimize environmental contamination. Waste storage and disposal facilities should comply with applicable federal, state, and local regulations.

The location of long-term and short-term storage for field records, and the measures to ensure the integrity of the data should be specified.

3.2 EQUIPMENT/INSTRUMENTATION

The equipment, instrumentation, and supplies at the sampling site should be specified and should be appropriate to accomplish the activities planned. The equipment and instrumentation should meet the requirements of specifications, methods, and procedures as specified in the QAPjP.

3.3 OPERATING PROCEDURES

The QAPjP should describe or make reference to all field activities that may affect data quality. For routinely performed activities, standard operating procedures (SOPs) are often prepared to ensure consistency and to save time and effort in preparing QAPjPs. Any deviation from an established procedure during a data collection activity should be documented. The procedures should be available for the indicated activities, and should include, at a minimum, the information described below.

3.3.1 Sample Management

The numbering and labeling system, chain-of-custody procedures, and how the samples are to be tracked from collection to shipment or receipt by the laboratory should be specified. Sample management procedures should also specify the holding times, volumes of sample required by the laboratory, required preservatives, and shipping requirements.

3.3.2 Reagent/Standard Preparation

The procedures describing how to prepare standards and reagents should be specified. Information concerning specific grades of materials used in reagent and standard preparation, appropriate glassware and containers for preparation and storage, and labeling and record keeping for stocks and dilutions should be included.

3.3.3 Decontamination

The procedures describing decontamination of field equipment before and during the sample collection process should be specified. These procedures should include cleaning materials used, the order of washing and rinsing with the cleaning materials, requirements for protecting or covering cleaned equipment, and procedures for disposing of cleaning materials.

3.3.4 Sample Collection

The procedures describing how the sampling operations are actually performed in the field should be specified. A simple reference to standard methods is not sufficient, unless a procedure is performed exactly as described in the published method. Methods from source documents published by the EPA, American Society for Testing and Materials, U.S. Department of the Interior, National Water Well Association, American Petroleum Institute, or other recognized organizations with appropriate expertise should be used, if possible. The procedures for sample collection should include at least the following:

- Applicability of the procedure,
- Equipment required,
- Detailed description of procedures to be followed in collecting the samples,
- Common problems encountered and corrective actions to be followed, and
- Precautions to be taken.

3.3.5 Field Measurements

The procedures describing all methods used in the field to determine a chemical or physical parameter should be described in detail. The procedures should address criteria from Section 4, as appropriate.

3.3.6 Equipment Calibration And Maintenance

The procedures describing how to ensure that field equipment and instrumentation are in working order should be specified. These describe calibration procedures and schedules, maintenance procedures and schedules, maintenance logs, and service arrangements for equipment. Calibration and maintenance of field equipment and instrumentation should be in accordance with manufacturers' specifications or applicable test specifications and should be documented.

3.3.7 Corrective Action

The procedures describing how to identify and correct deficiencies in the sample collection process should be specified. These should include specific steps to take in correcting deficiencies such as performing additional decontamination of equipment, resampling, or additional training of field personnel. The procedures should specify that each corrective action should be documented with a description of the deficiency and the corrective action taken, and should include the person(s) responsible for implementing the corrective action.

3.3.8 Data Reduction and Validation

The procedures describing how to compute results from field measurements and to review and validate these data should be specified. They should include all formulas used to calculate results and procedures used to independently verify that field measurement results are correct.

3.3.9 Reporting

The procedures describing the process for reporting the results of field activities should be specified.

3.3.10 Records Management

The procedures describing the means for generating, controlling, and archiving project-specific records and field operations records should be specified. These procedures should detail record generation and control and the requirements for record retention, including type, time, security, and retrieval and disposal authorities.

Project-specific records relate to field work performed for a project. These records may include correspondence, chain-of-custody records, field notes, all reports issued as a result of the work, and procedures used.

Field operations records document overall field operations and may include equipment performance and maintenance logs, personnel files, general field procedures, and corrective action reports.

3.3.11 Waste Disposal

The procedures describing the methods for disposal of waste materials resulting from field operations should be specified.

3.4 FIELD QA AND QC REQUIREMENTS

The QAPjP should describe how the following elements of the field QC program will be implemented.

3.4.1 Control Samples

Control samples are QC samples that are introduced into a process to monitor the performance of the system. Control samples, which may include blanks (e.g., trip, equipment, and laboratory), duplicates, spikes, analytical standards, and reference materials, can be used in different phases of the data collection process beginning with sampling and continuing through transportation, storage, and analysis.

Each day of sampling, at least one field duplicate and one equipment rinsate should be collected for each matrix sampled. If this frequency is not appropriate for the sampling equipment and method, then the appropriate changes

should be clearly identified in the QAPjP. When samples are collected for volatile organic analysis, a trip blank is also recommended for each day that samples are collected. In addition, for each sampling batch (20 samples of one matrix type), enough volume should be collected for at least one sample so as to allow the laboratory to prepare one matrix spike and either one matrix duplicate or one matrix spike duplicate for each analytical method employed. This means that the following control samples are recommended:

- Field duplicate (one per day per matrix type)
- Equipment rinsate (one per day per matrix type)
- Trip blank (one per day, volatile organics only)
- Matrix spike (one per batch [20 samples of each matrix type])
- Matrix duplicate or matrix spike duplicate (one per batch)

Additional control samples may be necessary in order to assure data quality to meet the project-specific DQOs.

3.4.2 Acceptance Criteria

Procedures should be in place for establishing acceptance criteria for field activities described in the QAPjP. Acceptance criteria may be qualitative or quantitative. Field events or data that fall outside of established acceptance criteria may indicate a problem with the sampling process that should be investigated.

3.4.3 Deviations

All deviations from plan should be documented as to the extent of, and reason for, the deviation. Any activity not performed in accordance with procedures or QAPjPs is considered a deviation from plan. Deviations from plan may or may not affect data quality.

3.4.4 Corrective Action

Errors, deficiencies, deviations, certain field events, or data that fall outside established acceptance criteria should be investigated. In some instances, corrective action may be needed to resolve the problem and restore proper functioning to the system. The investigation of the problem and any subsequent corrective action taken should be documented.

3.4.5 Data Handling

All field measurement data should be reduced according to protocols described or referenced in the QAPjP. Computer programs used for data reduction should be validated before use and verified on a regular basis. All information used in the calculations should be recorded to enable reconstruction of the final result at a later date.

Data should be reported in accordance with the requirements of the end-user as described in the QAPjP.

3.5 QUALITY ASSURANCE REVIEW

The QA Review consists of internal and external assessments to ensure that QA/QC procedures are in use and to ensure that field staff conform to these procedures. QA review should be conducted as deemed appropriate and necessary.

3.6 FIELD RECORDS

Records provide the direct evidence and support for the necessary technical interpretations, judgments, and discussions concerning project activities. These records, particularly those that are anticipated to be used as evidentiary data, should directly support current or ongoing technical studies and activities and should provide the historical evidence needed for later reviews and analyses. Records should be legible, identifiable, and retrievable and protected against damage, deterioration, or loss. The discussion in this section (3.6) outlines recommended procedures for record keeping. Organizations which conduct field sampling should develop appropriate record keeping procedures which satisfy relevant technical and legal requirements.

Field records generally consist of bound field notebooks with prenumbered pages, sample collection forms, personnel qualification and training forms, sample location maps, equipment maintenance and calibration forms, chain-of-custody forms, sample analysis request forms, and field change request forms. All records should be written in indelible ink.

Procedures for reviewing, approving, and revising field records should be clearly defined, with the lines of authority included. It is recommended that all documentation errors should be corrected by drawing a single line through the error so it remains legible and should be initialed by the responsible individual, along with the date of change. The correction should be written adjacent to the error.

Records should include (but are not limited to) the following:

Calibration Records & Traceability of Standards/Reagents -- Calibration is a reproducible reference point to which all sample measurements can be correlated. A sound calibration program should include provisions for documentation of frequency, conditions, standards, and records reflecting the calibration history of a measurement system. The accuracy of the calibration standards is important because all data will be in reference to the standards used. A program for verifying and documenting the accuracy of all working standards against primary grade standards should be routinely followed.

Sample Collection -- To ensure maximum utility of the sampling effort and resulting data, documentation of the sampling protocol, as performed in the field, is essential. It is recommended that sample collection records contain, at a minimum, the names of persons conducting the activity, sample number, sample location, equipment used, climatic conditions, documentation of adherence to protocol, and unusual observations. The

actual sample collection record is usually one of the following: a bound field notebook with prenumbered pages, a pre-printed form, or digitized information on a computer tape or disc.

Chain-of-Custody Records -- The chain-of-custody involving the possession of samples from the time they are obtained until they are disposed or shipped off-site should be documented as specified in the QAPjP and should include the following information: (1) the project name; (2) signatures of samplers; (3) the sample number, date and time of collection, and grab or composite sample designation; (4) signatures of individuals involved in sample transfer; and (5) if applicable, the air bill or other shipping number.

Maps and Drawings -- Project planning documents and reports often contain maps. The maps are used to document the location of sample collection points and monitoring wells and as a means of presenting environmental data. Information used to prepare maps and drawings is normally obtained through field surveys, property surveys, surveys of monitoring wells, aerial photography or photogrammetric mapping. The final, approved maps and/or drawings should have a revision number and date and should be subject to the same controls as other project records.

QC Samples -- Documentation for generation of QC samples, such as trip and equipment rinsate blanks, duplicate samples, and any field spikes should be maintained.

Deviations -- All deviations from procedural documents and the QAPjP should be recorded in the site logbook.

Reports -- A copy of any report issued and any supporting documentation should be retained.

4.0 LABORATORY OPERATIONS

The laboratory should conduct its operations in such a way as to provide reliable information. To achieve this, certain minimal policies and procedures should be implemented.

4.1 FACILITIES

The QAPjP should address all facility-related issues that may impact project data quality. Each laboratory should be of suitable size and construction to facilitate the proper conduct of the analyses. Adequate bench space or working area per analyst should be provided. The space requirement per analyst depends on the equipment or apparatus that is being utilized, the number of samples that the analyst is expected to handle at any one time, and the number of operations that are to be performed concurrently by a single analyst. Other issues to be considered include, but are not limited to, ventilation, lighting,

control of dust and drafts, protection from extreme temperatures, and access to a source of stable power.

Laboratories should be designed so that there is adequate separation of functions to ensure that no laboratory activity has an adverse effect on the analyses. The laboratory may require specialized facilities such as a perchloric acid hood or glovebox.

Separate space for laboratory operations and appropriate ancillary support should be provided, as needed, for the performance of routine and specialized procedures.

As necessary to ensure secure storage and prevent contamination or misidentification, there should be adequate facilities for receipt and storage of samples. The level of custody required and any special requirements for storage such as refrigeration should be described in planning documents.

Storage areas for reagents, solvents, standards, and reference materials should be adequate to preserve their identity, concentration, purity, and stability.

Adequate facilities should be provided for the collection and storage of all wastes, and these facilities should be operated so as to minimize environmental contamination. Waste storage and disposal facilities should comply with applicable federal, state, and local regulations.

The location of long-term and short-term storage of laboratory records and the measures to ensure the integrity of the data should be specified.

4.2 EQUIPMENT/INSTRUMENTATION

Equipment and instrumentation should meet the requirements and specifications of the specific test methods and other procedures as specified in the QAPjP. The laboratory should maintain an equipment/instrument description list that includes the manufacturer, model number, year of purchase, accessories, and any modifications, updates, or upgrades that have been made.

4.3 OPERATING PROCEDURES

The QAPjP should describe or make reference to all laboratory activities that may affect data quality. For routinely performed activities, SOPs are often prepared to ensure consistency and to save time and effort in preparing QAPjPs. Any deviation from an established procedure during a data collection activity should be documented. It is recommended that procedures be available for the indicated activities, and include, at a minimum, the information described below.

4.3.1 Sample Management

The procedures describing the receipt, handling, scheduling, and storage of samples should be specified.

Sample Receipt and Handling -- These procedures describe the precautions to be used in opening sample shipment containers and how to verify that chain-of-custody has been maintained, examine samples for damage, check for proper preservatives and temperature, and log samples into the laboratory sample streams.

Sample Scheduling -- These procedures describe the sample scheduling in the laboratory and includes procedures used to ensure that holding time requirements are met.

Sample Storage -- These procedures describe the storage conditions for all samples, verification and documentation of daily storage temperature, and how to ensure that custody of the samples is maintained while in the laboratory.

4.3.2 Reagent/Standard Preparation

The procedures describing how to prepare standards and reagents should be specified. Information concerning specific grades of materials used in reagent and standard preparation, appropriate glassware and containers for preparation and storage, and labeling and recordkeeping for stocks and dilutions should be included.

4.3.3 General Laboratory Techniques

The procedures describing all essentials of laboratory operations that are not addressed elsewhere should be specified. These techniques should include, but are not limited to, glassware cleaning procedures, operation of analytical balances, pipetting techniques, and use of volumetric glassware.

4.3.4 Test Methods

Procedures for test methods describing how the analyses are actually performed in the laboratory should be specified. A simple reference to standard methods is not sufficient, unless the analysis is performed exactly as described in the published method. Whenever methods from SW-846 are not appropriate, recognized methods from source documents published by the EPA, American Public Health Association (APHA), American Society for Testing and Materials (ASTM), the National Institute for Occupational Safety and Health (NIOSH), or other recognized organizations with appropriate expertise should be used, if possible. The documentation of the actual laboratory procedures for analytical methods should include the following:

Sample Preparation and Analysis Procedures -- These include applicable holding time, extraction, digestion, or preparation steps as appropriate to the method; procedures for determining the appropriate dilution to

analyze; and any other information required to perform the analysis accurately and consistently.

Instrument Standardization -- This includes concentration(s) and frequency of analysis of calibration standards, linear range of the method, and calibration acceptance criteria.

Sample Data -- This includes recording requirements and documentation including sample identification number, analyst, data verification, date of analysis and verification, and computational method(s).

Precision and Bias -- This includes all analytes for which the method is applicable and the conditions for use of this information.

Detection and Reporting Limits -- This includes all analytes in the method.

Test-Specific QC -- This describes QC activities applicable to the specific test and references any applicable QC procedures.

4.3.5 Equipment Calibration and Maintenance

The procedures describing how to ensure that laboratory equipment and instrumentation are in working order should be specified. These procedures include calibration procedures and schedules, maintenance procedures and schedules, maintenance logs, service arrangements for all equipment, and spare parts available in-house. Calibration and maintenance of laboratory equipment and instrumentation should be in accordance with manufacturers' specifications or applicable test specifications and should be documented.

4.3.6 QC

The type, purpose, and frequency of QC samples to be analyzed in the laboratory and the acceptance criteria should be specified. Information should include the applicability of the QC sample to the analytical process, the statistical treatment of the data, and the responsibility of laboratory staff and management in generating and using the data. Further details on development of project-specific QC protocols are described in Section 4.4.

4.3.7 Corrective Action

The procedures describing how to identify and correct deficiencies in the analytical process should be specified. These should include specific steps to take in correcting the deficiencies such as preparation of new standards and reagents, recalibration and restandardization of equipment, reanalysis of samples, or additional training of laboratory personnel in methods and procedures. The procedures should specify that each corrective action should be documented with a description of the deficiency and the corrective action taken, and should include the person(s) responsible for implementing the corrective action.

4.3.8 Data Reduction and Validation

The procedures describing how to review and validate the data should be specified. They should include procedures for computing and interpreting the results from QC samples, and independent procedures to verify that the analytical results are reported correctly. In addition, routine procedures used to monitor precision and bias, including evaluations of reagent, equipment rinsate, and trip blanks, calibration standards, control samples, duplicate and matrix spike samples, and surrogate recovery, should be detailed in the procedures. More detailed validation procedures should be performed when required in the contract or QAPjP.

4.3.9 Reporting

The procedures describing the process for reporting the analytical results should be specified.

4.3.10 Records Management

The procedures describing the means for generating, controlling, and archiving laboratory records should be specified. The procedures should detail record generation and control, and the requirements for record retention, including type, time, security, and retrieval and disposal authorities.

Project-specific records may include correspondence, chain-of-custody records, request for analysis, calibration data records, raw and finished analytical and QC data, data reports, and procedures used.

Laboratory operations records may include laboratory notebooks, instrument performance logs and maintenance logs in bound notebooks with prenumbered pages; laboratory benchsheets; software documentation; control charts; reference material certification; personnel files; laboratory procedures; and corrective action reports.

4.3.11 Waste Disposal

The procedures describing the methods for disposal of chemicals including standard and reagent solutions, process waste, and samples should be specified.

4.4 LABORATORY QA AND QC PROCEDURES

The QAPjP should describe how the following required elements of the laboratory QC program are to be implemented.

4.4.1 Method Proficiency

Procedures should be in place for demonstrating proficiency with each analytical method routinely used in the laboratory. These should include procedures for demonstrating the precision and bias of the method as performed by the laboratory and procedures for determining the method detection limit

(MDL). All terminology, procedures and frequency of determinations associated with the laboratory's establishment of the MDL and the reporting limit should be well-defined and well-documented. Documented precision, bias, and MDL information should be maintained for all methods performed in the laboratory.

4.4.2 Control Limits

Procedures should be in place for establishing and updating control limits for analysis. Control limits should be established to evaluate laboratory precision and bias based on the analysis of control samples. Typically, control limits for bias are based on the historical mean recovery plus or minus three standard deviation units, and control limits for precision range from zero (no difference between duplicate control samples) to the historical mean relative percent difference plus three standard deviation units. Procedures should be in place for monitoring historical performance and should include graphical (control charts) and/or tabular presentations of the data.

4.4.3 Laboratory Control Procedures

Procedures should be in place for demonstrating that the laboratory is in control during each data collection activity. Analytical data generated with laboratory control samples that fall within prescribed limits are judged to be generated while the laboratory was in control. Data generated with laboratory control samples that fall outside the established control limits are judged to be generated during an "out-of-control" situation. These data are considered suspect and should be repeated or reported with qualifiers.

Laboratory Control Samples -- Laboratory control samples should be analyzed for each analytical method when appropriate for the method. A laboratory control sample consists of either a control matrix spiked with analytes representative of the target analytes or a certified reference material.

Laboratory control sample(s) should be analyzed with each batch of samples processed to verify that the precision and bias of the analytical process are within control limits. The results of the laboratory control sample(s) are compared to control limits established for both precision and bias to determine usability of the data.

Method Blank -- When appropriate for the method, a method blank should be analyzed with each batch of samples processed to assess contamination levels in the laboratory. Guidelines should be in place for accepting or rejecting data based on the level of contamination in the blank.

Procedures should be in place for documenting the effect of the matrix on method performance. When appropriate for the method, there should be at least one matrix spike and either one matrix duplicate or one matrix spike duplicate per analytical batch. Additional control samples may be necessary to assure data quality to meet the project-specific DQOs.

Matrix-Specific Bias -- Procedures should be in place for determining the bias of the method due to the matrix. These procedures should include preparation and analysis of matrix spikes, selection and use of surrogates for organic methods, and the method of standard additions for metal and inorganic methods. When the concentration of the analyte in the sample is greater than 0.1%, no spike is necessary.

Matrix-Specific Precision -- Procedures should be in place for determining the precision of the method for a specific matrix. These procedures should include analysis of matrix duplicates and/or matrix spike duplicates. The frequency of use of these techniques should be based on the DQO for the data collection activity.

Matrix-Specific Detection Limit -- Procedures should be in place for determining the MDL for a specific matrix type (e.g., wastewater treatment sludge, contaminated soil, etc).

4.4.4 Deviations

Any activity not performed in accordance with laboratory procedures or QAPjPs is considered a deviation from plan. All deviations from plan should be documented as to the extent of, and reason for, the deviation.

4.4.5 Corrective Action

Errors, deficiencies, deviations, or laboratory events or data that fall outside of established acceptance criteria should be investigated. In some instances, corrective action may be needed to resolve the problem and restore proper functioning to the analytical system. The investigation of the problem and any subsequent corrective action taken should be documented.

4.4.6 Data Handling

Data resulting from the analyses of samples should be reduced according to protocols described in the laboratory procedures. Computer programs used for data reduction should be validated before use and verified on a regular basis. All information used in the calculations (e.g., raw data, calibration files, tuning records, results of standard additions, interference check results, and blank- or background-correction protocols) should be recorded in order to enable reconstruction of the final result at a later date. Information on the preparation of the sample (e.g., weight or volume of sample used, percent dry weight for solids, extract volume, dilution factor used) should also be maintained in order to enable reconstruction of the final result at a later date.

All data should be reviewed by a second analyst or supervisor according to laboratory procedures to ensure that calculations are correct and to detect transcription errors. Spot checks should be performed on computer calculations to verify program validity. Errors detected in the review process should be referred to the analyst(s) for corrective action. Data should be reported in accordance with the requirements of the end-user. It is recommended that the supporting documentation include at a minimum:

- Laboratory name and address.
- Sample information (including unique sample identification, sample collection date and time, date of sample receipt, and date(s) of sample preparation and analysis).
- Analytical results reported with an appropriate number of significant figures.
- Detection limits that reflect dilutions, interferences, or correction for equivalent dry weight.
- Method reference.
- Appropriate QC results (correlation with sample batch should be traceable and documented).
- Data qualifiers with appropriate references and narrative on the quality of the results.

4.5 QUALITY ASSURANCE REVIEW

The QA review consists of internal and external assessments to ensure that QA/QC procedures are in use and to ensure that laboratory staff conform to these procedures. QA review should be conducted as deemed appropriate and necessary.

4.6 LABORATORY RECORDS

Records provide the direct evidence and support for the necessary technical interpretations, judgements, and discussions concerning project activities. These records, particularly those that are anticipated to be used as evidentiary data, should directly support technical studies and activities, and provide the historical evidence needed for later reviews and analyses. Records should be legible, identifiable, and retrievable, and protected against damage, deterioration, or loss. The discussion in this section (4.6) outlines recommended procedures for record keeping. Organizations which conduct field sampling should develop appropriate record keeping procedures which satisfy relevant technical and legal requirements.

Laboratory records generally consist of bound notebooks with prenumbered pages, personnel qualification and training forms, equipment maintenance and calibration forms, chain-of-custody forms, sample analysis request forms, and analytical change request forms. All records should be written in indelible ink.

Procedures for reviewing, approving, and revising laboratory records should be clearly defined, with the lines of authority included. Any documentation errors should be corrected by drawing a single line through the error so that it remains legible and should be initialed by the responsible individual, along with the date of change. The correction is written adjacent to the error.

Strip-chart recorder printouts should be signed by the person who performed the instrumental analysis. If corrections need to be made in computerized data, a system parallel to the corrections for handwritten data should be in place.

Records of sample management should be available to permit the re-creation of an analytical event for review in the case of an audit or investigation of a dubious result.

Laboratory records should include, at least, the following:

Operating Procedures -- Procedures should be available to those performing the task outlined. Any revisions to laboratory procedures should be written, dated, and distributed to all affected individuals to ensure implementation of changes. Areas covered by operating procedures are given in Sections 3.3 and 4.3.

Quality Assurance Plans -- The QAPjP should be on file.

Equipment Maintenance Documentation -- A history of the maintenance record of each system serves as an indication of the adequacy of maintenance schedules and parts inventory. As appropriate, the maintenance guidelines of the equipment manufacturer should be followed. When maintenance is necessary, it should be documented in either standard forms or in logbooks. Maintenance procedures should be clearly defined and written for each measurement system and required support equipment.

Proficiency -- Proficiency information on all compounds reported should be maintained and should include (1) precision; (2) bias; (3) method detection limits; (4) spike recovery, where applicable; (5) surrogate recovery, where applicable; (6) checks on reagent purity, where applicable; and (7) checks on glassware cleanliness, where applicable.

Calibration Records & Traceability of Standards/Reagents -- Calibration is a reproducible reference point to which all sample measurements can be correlated. A sound calibration program should include provisions for documenting frequency, conditions, standards, and records reflecting the calibration history of a measurement system. The accuracy of the calibration standards is important because all data will be in reference to the standards used. A program for verifying and documenting the accuracy and traceability of all working standards against appropriate primary grade standards or the highest quality standards available should be routinely followed.

Sample Management -- All required records pertaining to sample management should be maintained and updated regularly. These include chain-of-custody forms, sample receipt forms, and sample disposition records.

Original Data -- The raw data and calculated results for all samples should be maintained in laboratory notebooks, logs, benchsheets, files or other sample tracking or data entry forms. Instrumental output should be stored in a computer file or a hardcopy report.

QC Data -- The raw data and calculated results for all QC and field samples and standards should be maintained in the manner described in the preceding paragraph. Documentation should allow correlation of sample results with associated QC data. Documentation should also include the source and lot numbers of standards for traceability. QC samples include, but are not limited to, control samples, method blanks, matrix spikes, and matrix spike duplicates.

Correspondence -- Project correspondence can provide evidence supporting technical interpretations. Correspondence pertinent to the project should be kept and placed in the project files.

Deviations -- All deviations from procedural and planning documents should be recorded in laboratory notebooks. Deviations from QAPjPs should be reviewed and approved by the authorized personnel who performed the original technical review or by their designees.

Final Report -- A copy of any report issued and any supporting documentation should be retained.

5.0 DEFINITIONS

The following terms are defined for use in this document:

ACCURACY — The closeness of agreement between an observed value and an accepted reference value. When applied to a set of observed values, accuracy will be a combination of a random component and of a common systematic error (or bias) component.

BATCH: — A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit (see Section 3.4.1 for field samples and Section 4.4.3 for laboratory samples). For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

BIAS: — The deviation due to matrix effects of the measured value ($x_s - x_u$) from a known spiked amount. Bias can be assessed by comparing a measured value to an accepted reference value in a sample of known concentration or by determining the recovery of a known amount of contaminant spiked into a sample (matrix spike). Thus, the bias (B) due to matrix effects based on a matrix spike is calculated as:

$$B = (x_s - x_u) - K$$

where:

x_s = measured value for spiked sample,
x_u = measured value for unspiked sample, and
K = known value of the spike in the sample.

Using the following equation yields the percent recovery (%R).

$$\%R = 100\ (x_s - x_u)/\ K$$

BLANK: see Equipment Rinsate, Method Blank, Trip Blank.

CONTROL SAMPLE: A QC sample introduced into a process to monitor the performance of the system.

DATA QUALITY OBJECTIVES (DQOs): A statement of the overall level of uncertainty that a decision-maker is willing to accept in results derived from environmental data (see reference 2, EPA/QAMS, July 16, 1986). This is qualitatively distinct from quality measurements such as precision, bias, and detection limit.

DATA VALIDATION: The process of evaluating the available data against the project DQOs to make sure that the objectives are met. Data validation may be very rigorous, or cursory, depending on project DQOs. The available data reviewed will include analytical results, field QC data and lab QC data, and may also include field records.

DUPLICATE: see Matrix Duplicate, Field Duplicate, Matrix Spike Duplicate.

EQUIPMENT BLANK: see Equipment Rinsate.

EQUIPMENT RINSATE: A sample of analyte-free media which has been used to rinse the sampling equipment. It is collected after completion of decontamination and prior to sampling. This blank is useful in documenting adequate decontamination of sampling equipment.

ESTIMATED QUANTITATION LIMIT (EQL): The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected as the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs in SW-846 are provided for guidance and may not always be achievable.

FIELD DUPLICATES: Independent samples which are collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed independently. These duplicates are useful in documenting the precision of the sampling process.

LABORATORY CONTROL SAMPLE: A known matrix spiked with compound(s) representative of the target analytes. This is used to document laboratory performance.

MATRIX: The component or substrate (e.g., surface water, drinking water) which contains the analyte of interest.

MATRIX DUPLICATE: An intralaboratory split sample which is used to document the precision of a method in a given sample matrix.

MATRIX SPIKE: An aliquot of sample spiked with a known concentration of target analyte(s). The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample matrix.

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

METHOD BLANK: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank should be carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

For a method blank to be acceptable for use with the accompanying samples, the concentration in the blank of any analyte of concern should not be higher than the highest of either:

(1)The method detection limit, or

(2)Five percent of the regulatory limit for that analyte, or

(3)Five percent of the measured concentration in the sample.

METHOD DETECTION LIMIT (MDL): The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from

analysis of a sample in a given matrix type containing the analyte.

For operational purposes, when it is necessary to determine the MDL in the matrix, the MDL should be determined by multiplying the appropriate one-sided 99% t-statistic by the standard deviation obtained from a minimum of three analyses of a matrix spike containing the analyte of interest at a concentration three to five times the estimated MDL, where the t-statistic is obtained from standard references or the table below.

No. of samples:	t-statistic
3	6.96
4	4.54
5	3.75
6	3.36
7	3.14
8	3.00
9	2.90
10	2.82

Estimate the MDL as follows:
Obtain the concentration value that corresponds to:

a) an instrument signal/noise ratio within the range of 2.5 to 5.0, or

b) the region of the standard curve where there is a significant change in sensitivity (i.e., a break in the slope of the standard curve).

Determine the variance (S^2) for each analyte as follows:

$$s^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} (x_i - \bar{x})^2\right]$$

where x_i = the ith measurement of the variable x
and $\bar{x}$ = the average value of x;

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$$

Determine the standard deviation (s) for each analyte as follows:

$$s = (S^2)^{1/2}$$

Determine the MDL for each analyte as follows:

$$MDL = t_{(n-1,\ \alpha = .99)}(s)$$

where $t_{(n-1,\ \alpha = .99)}$ is the one-sided t-statistic appropriate for the number of samples used to determine (s), at the 99 percent level.

ORGANIC-FREE REAGENT WATER:

For volatiles, all references to water in the methods refer to water in which an interferant is not observed at the method detection limit of the compounds of interest. Organic-free reagent water can be generated by passing tap water through a carbon filter bed containing about 1 pound of activated carbon. A water purification system may be used to generate organic-free deionized water. Organic-free reagent water may also be prepared by boiling water for 15 minutes and, subsequently, while maintaining the temperature at 90°C, bubbling a contaminant-free inert gas through the water for 1 hour.

For semivolatiles and nonvolatiles, all references to water in the methods refer to water in which an interferant is not observed at the method detection limit of the compounds of interest. Organic-free reagent water can be generated by passing tap water through a carbon filter bed containing about 1 pound of activated carbon. A water purification system may be used to generate organic-free deionized water.

PRECISION:

The agreement among a set of replicate measurements without assumption of knowledge of the true value. Precision is estimated by means of duplicate/replicate analyses. These samples should contain concentrations of analyte above the MDL, and may involve the use of matrix spikes. The most commonly used estimates of precision are the relative standard deviation (RSD) or the coefficient of variation (CV),

$$RSD = CV = 100\ S/\bar{x},$$

where:
$\bar{x}$ = the arithmetic mean of the x_i measurements, and S = variance; and the relative percent difference (RPD) when only two samples are available.

$$RPD = 100\ [(x_1 - x_2)/((x_1 + x_2)/2)].$$

PROJECT: Single or multiple data collection activities that are related through the same planning sequence.

QUALITY ASSURANCE PROJECT PLAN (QAPjP): An orderly assemblage of detailed procedures designed to produce data of sufficient quality to meet the data quality objectives for a specific data collection activity.

RCRA: The Resource Conservation and Recovery Act.

REAGENT BLANK: See Method Blank.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

SPLIT SAMPLES: Aliquots of sample taken from the same container and analyzed independently. In cases where aliquots of samples are impossible to obtain, field duplicate samples should be taken for the matrix duplicate analysis. These are usually taken after mixing or compositing and are used to document intra- or interlaboratory precision.

STANDARD ADDITION: The practice of adding a known amount of an analyte to a sample immediately prior to analysis. It is typically used to evaluate interferences.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate

section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

SURROGATE: An organic compound which is similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples.

TRIP BLANK: A sample of analyte-free media taken from the laboratory to the sampling site and returned to the laboratory unopened. A trip blank is used to document contamination attributable to shipping and field handling procedures. This type of blank is useful in documenting contamination of volatile organics samples.

6.0 REFERENCES

1. Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans, QAMS-005/80, December 29, 1980, Office of Monitoring Systems and Quality Assurance, ORD, U.S. EPA, Washington, DC 20460.

2. Development of Data Quality Objectives, Description of Stages I and II, July 16, 1986, Quality Assurance Management Staff, ORD, U.S. EPA, Washington, DC 20460.

3. RCRA Ground-Water Monitoring Technical Enforcement Guidance Document, September, 1986, Office of Waste Programs Enforcement. OSWER, U.S. EPA, Washington, DC, 20460.

4. DQO Training Software, Version 6.5, December, 1988, Quality Assurance Management Staff, ORD, U.S. EPA, Washington, DC 20460.

5. Preparing Perfect Project Plans, EPA/600/9-89/087, October 1989, Risk Reduction Engineering Laboratory (Guy Simes), Cincinnati OH.

6. ASTM Method D 1129-77, Specification for Reagent Water. 1991 Annual Book of ASTM Standards. Volume 11.01 Water and Environmental Technology.

7. Generation of Environmental Data Related to Waste Management Activities (Draft). February 1989. ASTM.

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* Definition of term.

CHAPTER FIVE

MISCELLANEOUS TEST METHODS

The following methods are found in Chapter Five:

Method 5050:	Bomb Preparation Method for Solid Waste
Method 9010A:	Total and Amenable Cyanide (Colorimetric, Manual)
Method 9012:	Total and Amenable Cyanide (Colorimetric, Automated UV)
Method 9013:	Cyanide Extraction Procedure for Solids and Oils
Method 9020B:	Total Organic Halides (TOX)
Method 9021:	Purgeable Organic Halides (POX)
Method 9022:	Total Organic Halides (TOX) by Neutron Activation Analysis
Method 9030A:	Acid-Soluble and Acid-Insoluble Sulfides
Method 9031:	Extractable Sulfides
Method 9035:	Sulfate (Colorimetric, Automated, Chloranilate)
Method 9036:	Sulfate (Colorimetric, Automated, Methylthymol Blue, AA II)
Method 9038:	Sulfate (Turbidimetric)
Method 9056:	Determination of Inorganic Anions by Ion Chromatography Method
Method 9060:	Total Organic Carbon
Method 9065:	Phenolics (Spectrophotometric, Manual 4-AAP with Distillation)
Method 9066:	Phenolics (Colorimetric, Automated 4-AAP with Distillation)
Method 9067:	Phenolics (Spectrophotometric, MBTH with Distillation)
Method 9070:	Total Recoverable Oil & Grease (Gravimetric, Separatory Funnel Extraction)
Method 9071A:	Oil and Grease Extraction Method for Sludge and Sediment Samples
Method 9075:	Test Method for Total Chlorine in New and Used Petroleum Products by X-Ray Fluorescence Spectrometry (XRF)
Method 9076:	Test Method for Total Chlorine in New and Used Petroleum Products by Oxidative Combustion and Microcoulometry
Method 9077:	Test Methods for Total Chlorine in New and Used Petroleum Products (Field Test Kit Methods)
Method 9131:	Total Coliform: Multiple Tube Fermentation Technique
Method 9132:	Total Coliform: Membrane Filter Technique
Method 9200:	Nitrate
Method 9250:	Chloride (Colorimetric, Automated Ferricyanide AAI)
Method 9251:	Chloride (Colorimetric, Automated FerricyanideAAII)
Method 9252A:	Chloride (Titrimetric, Mercuric Nitrate)
Method 9253:	Chloride (Titrimetric, Silver Nitrate)
Method 9320:	Radium-228

METHOD 5050

BOMB PREPARATION METHOD FOR SOLID WASTE

1.0 SCOPE AND APPLICATION

1.1 This method describes the sample preparation steps necessary to determine total chlorine in solid waste and virgin and used oils, fuels and related materials, including: crankcase, hydraulic, diesel, lubricating and fuel oils, and kerosene by bomb oxidation and titration or ion chromatography. Depending on the analytical finish chosen, other halogens (bromine and fluorine) and other elements (sulfur and nitrogen) may also be determined.

1.2 The applicable range of this method varies depending on the analytical finish chosen. In general, levels as low as 500 μg/g chlorine in the original oil sample can be determined. The upper range can be extended to percentage levels by dilution of the combustate.

1.3 This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific safety statements are given in Section 3.0.

2.0 SUMMARY OF METHOD

2.1 The sample is oxidized by combustion in a bomb containing oxygen under pressure. The liberated halogen compounds are absorbed in a sodium carbonate/sodium bicarbonate solution. Approximately 30 to 40 minutes are required to prepare a sample by this method. Samples with a high water content (> 25%) may not combust efficiently and may require the addition of a mineral oil to facilitate combustion. Complete combustion is still not guaranteed for such samples.

2.2 The bomb combustate solution can then be analyzed for the following elements as their anion species by one or more of the following methods:

Method	Title
9252	Chloride (Titrimetric, Mercuric Nitrate)
9253	Chloride (Titrimetric, Silver Nitrate)
9056	Inorganic Anions by Ion Chromatography (Chloride, Sulfate, Nitrate, Phosphate, Fluoride, Bromide)

NOTE: Strict adherence to all of the provisions prescribed hereinafter ensures against explosive rupture of the bomb, or a blowout, provided the bomb is of proper design and construction and in good mechanical condition. It is desirable, however, that the bomb be enclosed in a shield of steel plate at least 1/2 in. (12.7 mm) thick, or equivalent protection be provided against unforeseeable contingencies.

3.0 INTERFERENCES

3.1 Samples with very high water content (> 25%) may not combust efficiently and may require the addition of a mineral oil to facilitate combustion.

3.2 To determine total nitrogen in samples, the bombs must first be purged of ambient air. Otherwise, nitrogen results will be biased high.

4.0 APPARATUS AND MATERIALS

4.1 Bomb, having a capacity of not less than 300 mL, so constructed that it will not leak during the test, and that quantitative recovery of the liquids from the bomb may be readily achieved. The inner surface of the bomb may be made of stainless steel or any other material that will not be affected by the combustion process or products. Materials used in the bomb assembly, such as the head gasket and lead-wire insulation, shall be resistant to heat and chemical action and shall not undergo any reaction that will affect the chlorine content of the sample in the bomb.

4.2 Sample cup, platinum or stainless steel, 24 mm in outside diameter at the bottom, 27 mm in outside diameter at the top, 12 mm in height outside, and weighing 10 to 11 g.

4.3 Firing wire, platinum or stainless steel, approximately No. 26 B & S gage.

4.4 Ignition circuit, capable of supplying sufficient current to ignite the nylon thread or cotton wicking without melting the wire.

NOTE: The switch in the ignition circuit shall be of the type that remains open, except when held in closed position by the operator.

4.5 Nylon sewing thread, or Cotton Wicking, white.

4.6 Funnel, to fit a 100-mL volumetric flask.

4.7 Class A volumetric flasks, 100-mL, one per sample.

4.8 Syringe, 5- or 10-mL disposable plastic or glass.

4.9 Apparatus for specific analysis methods are given in the methods.

4.10 Analytical balance: capable of weighing to 0.0001 g.

5.0 REAGENTS

5.1 Purity of reagents. Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Oxygen. Free of combustible material and halogen compounds, available at a pressure of 40 atm.

WARNING: Oxygen vigorously accelerates combustion (see Appendix A1.1)

5.4 Sodium bicarbonate/sodium carbonate solution. Dissolve 2.5200 g $NaHCO_3$ and 2.5440 g Na_2CO_3 in reagent water and dilute to 1 L.

5.5 White oil. Refined.

5.6 Reagents and materials for specific analysis methods are given in the methods.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 Ensure that the portion of the sample used for the test is representative of the sample.

6.3 To minimize losses of volatile halogenated solvents that may be present in the sample, keep the field and laboratory samples as free of headspace as possible.

6.4 Because used oils may contain toxic and/or carcinogenic substances appropriate field and laboratory safety procedures should be followed.

7.0 PROCEDURE

7.1 Sample Preparation

7.1.1 Preparation of bomb and sample. Cut a piece of firing wire approximately 100 mm in length and attach the free ends to the terminals. Arrange the wire so that it will be just above and not touching the sample cup. Loop a cotton thread around the wire so that the ends will extend into the sampling cup. Pipet 10 mL of the $NaHCO_3/Na_2CO_3$ solution into the bomb, wetting the sides. Take an aliquot of the oil sample of approximately 0.5 g using a 5- or 10-mL disposable plastic syringe, and place in the sample cup. The actual sample weight is determined by the difference

between the weight of the empty and filled syringe. Do not use more than 1 g of sample.

NOTE: After repeated use of the bomb for chlorine determination, a film may be noticed on the inner surface. This dullness should be removed by periodic polishing of the bomb. A satisfactory method for doing this is to rotate the bomb in a lathe at about 300 rpm and polish the inside surface with Grit No. 2/0 or equivalent paper[1] coated with a light machine oil to prevent cutting, and then with a paste of grit-free chromic oxide[2] and water. This procedure will remove all but very deep pits and put a high polish on the surface. Before using the bomb, it should be washed with soap and water to remove oil or paste left from the polishing operation. Bombs with porous or pitted surfaces should never be used because of the tendency to retain chlorine from sample to sample.

NOTE: If the sample is not readily combustible, other nonvolatile, chlorine-free combustible diluents such as white oil may be employed. However, the combined weight of sample and nonvolatile diluent shall not exceed 1 g. Some solid additives are relatively insoluble but may be satisfactorily burned when covered with a layer of white oil.

NOTE: The practice of alternately running samples high and low in chlorine content should be avoided whenever possible. It is difficult to rinse the last traces of chlorine from the walls of the bomb, and the tendency for residual chlorine to carry over from sample to sample has been observed in a number of laboratories. When a sample high in chlorine has preceded one low in chlorine content, the test on the low-chlorine sample should be repeated, and one or both of the low values thus obtained should be considered suspect if they do not agree within the limits of repeatability of this method.

NOTE: Do not use more than 1 g total of sample and white oil or other chlorine-free combustible material. Use of excess amounts of these materials could cause a buildup of dangerously high pressure and possible rupture of the bomb.

7.1.2 Addition of oxygen. Place the sample cup in position and arrange the thread so that the end dips into the sample. Assemble the bomb and tighten the cover securely. Admit oxygen slowly (to avoid blowing the oil from the cup) until a pressure is reached as indicated in Table 1.

NOTE: Do not add oxygen or ignite the sample if the bomb has been jarred, dropped, or tiled.

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[1]Emery Polishing Paper grit No. 2/0 may be purchased from the Behr-Manning Co., Troy, NY.

[2]Chromic oxide may be purchased from J.T. Baker & Co., Phillipsburg, NJ.

7.1.3 Combustion. Immerse the bomb in a cold water bath. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. Remove the bomb from the bath after immersion for at least 10 minutes. Release the pressure at a slow, uniform rate such that the operation requires at least 1 min. Open the bomb and examine the contents. If traces of unburned oil or sooty deposits are found, discard the determination, and thoroughly clean the bomb before using it again.

7.1.4 Collection of halogen solution. Using reagent water and a funnel, thoroughly rinse the interior of the bomb, the sample cup, the terminals, and the inner surface of the bomb cover into a 100-mL volumetric flask. Dilute to the mark with reagent water.

7.1.5 Cleaning procedure for bomb and sample cup. Remove any residual fuse wire from the terminals and the cup. Using hot water, rinse the interior of the bomb, the sample cup, the terminals, and the inner surface of the bomb cover. (If any residue remains, first scrub the bomb with Alconox solution). Copiously rinse the bomb, cover, and cup with reagent water.

7.2 Sample Analysis. Analyze the combustate for chlorine or other halogens using the methods listed in Step 2.2. It may be necessary to dilute the samples so that the concentration will fall within the range of standards.

7.3 Calculations. Calculate the concentrations of each element detected in the sample according to the following equation:

$$C_o = \frac{C_{com} \times V_{com} \times DF}{W_o} \qquad (1)$$

where:

C_o = concentration of element in the sample, μg/g
C_{com} = concentration of element in the combustate, μg/mL
V_{com} = total volume of combustate, mL
DF = dilution factor
W_o = weight of sample combusted, g.

Report the concentration of each element detected in the sample in micrograms per gram.

Example: A 0.5-g oil sample was combusted, yielding 10 mL of combustate. The combustate was diluted to 100 mL total volume and analyzed for chloride, which was measured to be 5 μg/mL. The concentration of chlorine in the original sample is then calculated as shown below:

$$C_o = \frac{\frac{5\ \mu g}{mL} \times (10\ mL) \times (10)}{0.5\ g} \qquad (2)$$

$$C_o = 1{,}000\ \frac{\mu g}{g} \qquad (3)$$

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 One sample in ten should be bombed twice. The results should agree to within 10%, expressed as the relative percent difference of the results.

8.3 Analyze matrix spike and matrix spike duplicates - spike samples with the elements of interest at a level commensurate with the levels being determined. The spiked compounds should be similar to those expected in the sample. Any sample suspected of containing > 25% water should also be spiked with organic chlorine.

8.4 For higher levels (e.g., percent levels), spiking may be inappropriate. For these cases, samples of known composition should be combusted. The results should agree to within 10% of the expected result.

8.5 Quality control for the analytical method(s) of choice should be followed.

9.0 PERFORMANCE

See analytical methods referenced in Step 2.2.

10.0 REFERENCES

1. ASTM Method D 808-81, Standard Test Method for Chlorine in New and Used Petroleum Products (Bomb Method). 1988 Annual Book of ASTM Standards. Volume 05.01 Petroleum Products and Lubricants.

2. Gaskill, A.; Estes, E. D.; Hardison, D. L.; and Myers, L. E. Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels. Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA 80. July 1988.

TABLE 1.
GAGE PRESSURES

Capacity of bomb, mL	Minimum gage pressure[a], atm	Maximum gage pressure[a], atm
300 to 350	38	40
350 to 400	35	37
400 to 450	30	32
450 to 500	27	29

[a]The minimum pressures are specified to provide sufficient oxygen for complete combustion, and the maximum pressures represent a safety requirement. Refer to manufacturers' specifications for appropriate gage pressure, which may be lower than those listed here.

APPENDIX

A1. PRECAUTIONARY STATEMENTS

A1.1 Oxygen

Warning--Oxygen vigorously accelerates combustion.

Keep oil and grease away. Do not use oil or grease on regulators, gages, or control equipment.

Use only with equipment conditioned for oxygen service by careful cleaning to remove oil, grease, and other combustibles.

Keep combustibles away from oxygen and eliminate ignition sources.

Keep surfaces clean to prevent ignition or explosion, or both, on contact with oxygen.

Always use a pressure regulator. Release regulator tension before opening cylinder valve.

All equipment and containers used must be suitable and recommended for oxygen service.

Never attempt to transfer oxygen from cylinder in which it is received to any other cylinder. Do not mix gases in cylinders.

Do not drop cylinder. Make sure cylinder is secured at all times.

Keep cylinder valve closed when not in use.

Stand away from outlet when opening cylinder valve.

For technical use only. Do not use for inhalation purposes.

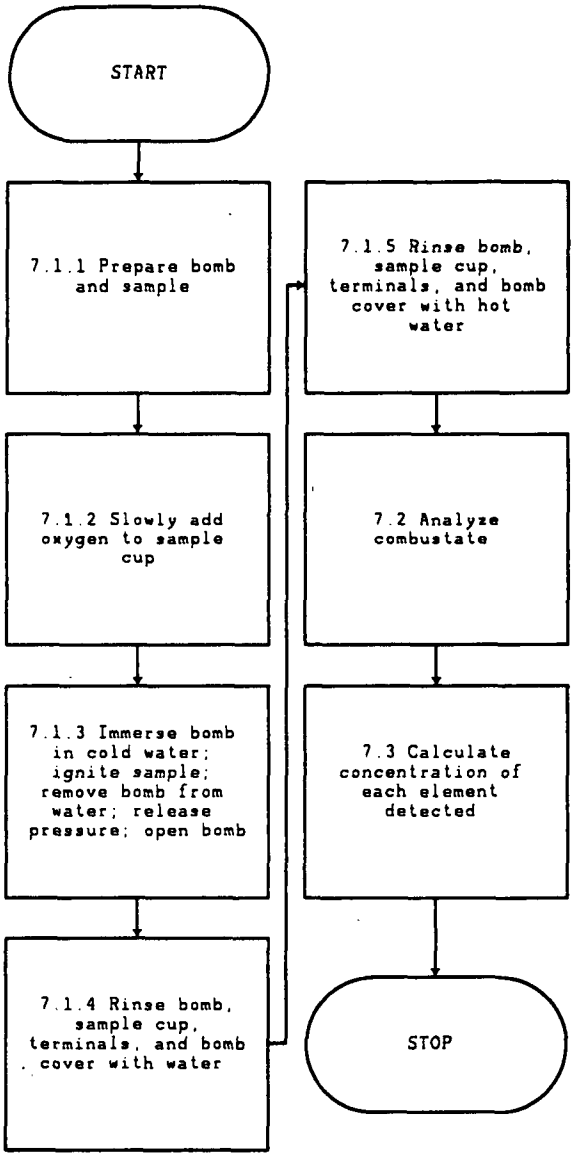
Keep cylinder out of sun and away from heat.

Keep cylinders from corrosive environment.

Do not use cylinder without label.

Do not use dented or damaged cylinders.

See Compressed Gas Association booklets G-4 and G4.1 for details of safe practice in the use of oxygen.


START
7.1.1 Prepare bomb and sample
7.1.2 Slowly add oxygen to sample cup
7.1.3 Immerse bomb in cold water; ignite sample; remove bomb from water; release pressure; open bomb
7.1.4 Rinse bomb, sample cup, terminals, and bomb cover with water
7.1.5 Rinse bomb, sample cup, terminals, and bomb cover with hot water
7.2 Analyze combustate
7.3 Calculate concentration of each element detected
STOP

METHOD 9010A

TOTAL AND AMENABLE CYANIDE

1.0 SCOPE AND APPLICATION

1.1 Method 9010 is used to determine the concentration of inorganic cyanide (CAS Registry Number 57-12-5) in wastes or leachate. The method detects inorganic cyanides that are present as either soluble salts or complexes. It is used to determine values for both total cyanide and cyanide amenable to chlorination. The "reactive" cyanide content of a waste, that is, the cyanide content that could generate toxic fumes when exposed to mild acidic conditions, is not distilled by Method 9010 (refer to Chapter Seven). However, Method 9010 is used to quantify the concentration of cyanide from the reactivity test.

1.2 The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide exceeding 0.1 mg/L (0.025 mg/250 mL of absorbing liquid).

1.3 The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

1.4 This method was designed to address the problem of "trace" analyses (<1000 ppm). The method may also be used for "minor" (1000 ppm - 10,000 ppm) and "major" (>10,000 ppm) analyses by adapting the sample preparation techniques or cell path length. However, the amount of sodium hydroxide in the standards and the sample analyzed must be the same.

2.0 SUMMARY OF METHOD

2.1 The cyanide, as hydrocyanic acid (HCN), is released from samples containing cyanide by means of a reflux-distillation operation under acidic conditions and absorbed in a scrubber containing sodium hydroxide solution. The cyanide in the absorbing solution is then determined colorimetrically or titrametrically.

2.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction of cyanide with chloramine-T at a pH less than 8. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read at 578 nm for the complex formed with pyridine-barbituric acid reagent and CNCl. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.3 The titration measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3.0 INTERFERENCES

3.1 Interferences are eliminated or reduced by using the distillation procedure. Chlorine and sulfide are interferences in Method 9010.

3.2 Oxidizing agents such as chlorine decompose most cyanides. Chlorine interferences can be removed by adding an excess of sodium arsenite to the waste prior to preservation and storage of the sample to reduce the chlorine to chloride which does not interfere.

3.3 Sulfide interference can be removed by adding an excess of bismuth nitrate to the waste (to precipitate the sulfide) before distillation. Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during the distillation should be treated by the addition of bismuth nitrate.

3.4 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds once formed will decompose under test conditions to generate HCN. The possibility of interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid just before distillation. Nitrate and nitrite are interferences when present at levels higher than 10 mg/L and in conjunction with certain organic compounds.

3.5 Thiocyanate is reported to be an interference when present at very high levels. Levels of 10 mg/L were not found to interfere.

3.6 Fatty acids, detergents, surfactants, and other compounds may cause foaming during the distillation when they are present in large concentrations and will make the endpoint of the titration difficult to detect. They may be extracted at pH 6-7.

4.0 APPARATUS AND MATERIALS

4.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of one liter size with inlet tube and provision for condenser. The gas scrubber may be a 270-mL Fisher-Milligan scrubber (Fisher, Part No. 07-513) or equivalent. The reflux apparatus may be a Wheaton 377160 distillation unit or equivalent.

4.2 Spectrophotometer - Suitable for measurements at 578 nm with a 1.0 cm cell or larger.

4.3 Hot plate stirrer/heating mantle.

4.4 pH meter.

4.5 Amber light.

4.6 Vacuum source.

4.7 Refrigerator.

4.8 5 mL microburette

4.9 7 Class A volumetric flasks - 100 and 250 mL

4.10 Erlenmeyer flask - 500 mL

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Reagents for sample collection, preservation, and handling

5.3.1 Sodium arsenite (0.1N), $NaAsO_2$. Dissolve 3.2 g $NaAsO_2$ in 250 mL water.

5.3.2 Ascorbic acid, $C_6H_8O_6$.

5.3.3 Sodium hydroxide solution (50%), NaOH. Commercially available.

5.3.4 Acetic acid (1.6M) CH_3COOH. Dilute one part of concentrated acetic acid with 9 parts of water.

5.3.5 2,2,4-Trimethylpentane, C_8H_{18}.

5.3.6 Hexane, C_6H_{14}.

5.3.7 Chloroform, $CHCl_3$.

5.4 Reagents for cyanides amenable to chlorination

5.4.1 Calcium hypochlorite solution (0.35M), $Ca(OCl)_2$. Combine 5 g of calcium hypochlorite and 100 mL of water. Shake before using.

5.4.2 Sodium hydroxide solution (1.25N), NaOH. Dissolve 50 g of NaOH in 1 liter of water.

5.4.3 Sodium arsenite (0.1N). See Step 5.3.1.

5.4.4 Potassium iodide starch paper.

5.5 Reagents for distillation

5.5.1 Sodium hydroxide (1.25N). See Step 5.4.2.

5.5.2 Bismuth nitrate (0.062M), $Bi(NO)_3 \cdot 5H_2O$. Dissolve 30 g $Bi(NO)_3 \cdot 5H_2O$ in 100 mL of water. While stirring, add 250 mL of glacial acetic acid, CH_3COOH. Stir until dissolved and dilute to 1 liter with water.

5.5.3 Sulfamic acid (0.4N), H_2NSO_3H. Dissolve 40 g H_2NSO_3H in 1 liter of water.

5.5.4 Sulfuric acid (18N), H_2SO_4. Slowly and carefully add 500 mL of concentrated H_2SO_4 to 500 mL of water.

5.5.5 Magnesium chloride solution (2.5M), $MgCl_2 \cdot 6H_2O$. Dissolve 510 g of $MgCl_2 \cdot 6H_2O$ in 1 liter of water.

5.5.6 Lead acetate paper.

5.6 Reagents for spectrophotometric determination

5.6.1 Sodium hydroxide solution (0.25N), NaOH. Dissolve 10 g NaOH in 1 liter of water.

5.6.2 Sodium phosphate monobasic (1M), $NaH_2PO_4 \cdot H_2O$. Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in 1 liter of water. Refrigerate this solution.

5.6.3 Chloramine-T solution (0.44%), $C_7H_7ClNNaO_2S$. Dissolve 1.0 g of white, water soluble chloramine-T in 100 mL of water and refrigerate until ready to use.

5.6.4 Pyridine-Barbituric acid reagent, $C_5H_5N \cdot C_4H_4N_2O_3$. Place 15 g of barbituric acid in a 250-mL volumetric flask and add just enough water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of concentrated hydrochloric acid (HCl), mix, and cool to room temperature. Dilute to 250 mL with water. This reagent is stable for approximately six months if stored in a cool, dark place.

5.6.5 Stock potassium cyanide solution (1 mL = 1000 μg CN^-), KCN. Dissolve 2.51 g of KCN and 2 g KOH in 900 mL of water. Standardize with 0.0192N silver nitrate, $AgNO_3$. Dilute to appropriate concentration to achieve 1 mL = 1000 μg of CN^-.

NOTE: Detailed procedure for $AgNO_3$ standardization is described in "Standard Methods for the Examination of Water and Wastewater", 16th Edition, (1985), Methods 412C and 407A.

5.6.6 Intermediate standard potassium cyanide solution, (1 mL = 100 μg CN^-), KCN. Dilute 100 mL of stock potassium cyanide solution (1 mL = 1000 μg CN^-) to 1000 mL with water.

5.6.7 Working standard potassium cyanide solution (1 mL = 10 μg CN^-), KCN. Prepare fresh daily by diluting 100 mL of intermediate standard potassium cyanide solution and 10 mL of 1N NaOH to 1 liter with water.

5.7 Reagents for titration procedure

5.7.1 Rhodanine indicator - Dissolve 20 mg of p-dimethylamino-benzal-rhodanine, $C_{12}H_{12}N_2OS_2$, in 100 mL of acetone.

5.7.2 Standard silver nitrate solution (0.0192N), $AgNO_3$. Prepare by crushing approximately 5 g $AgNO_3$ and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$. Dissolve in 1 liter of water.

NOTE: Detailed procedure for $AgNO_3$ standardization is described in "Standard Methods for the Examination of Water and Wastewater", 16th Edition, (1985), Methods 412C and 407A.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 Samples should be collected in plastic or glass containers. All containers must be thoroughly cleaned and rinsed.

6.3 Oxidizing agents such as chlorine decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with potassium iodide-starch test paper. A blue color indicates the need for treatment. Add 0.1N sodium arsenite solution a few mL at a time until a drop of sample produces no color on the indicator paper. Add an additional 5 mL of sodium arsenite solution for each liter of sample. Ascorbic acid can be used as an alternative although it is not as effective as arsenite. Add a few crystals of ascorbic acid at a time until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.

6.4 Aqueous samples must be preserved by adding 50% sodium hydroxide until the pH is greater than or equal to 12 at the time of collection.

6.5 Samples should be chilled to 4°C.

6.6 When properly preserved, cyanide samples can be stored for up to 14 days prior to sample preparation steps.

6.7 Solid and oily wastes may be extracted prior to analysis by method 9013. It uses a dilute NaOH solution (pH = 12) as the extractant. This yields extractable cyanide.

6.8 If fatty acids, detergents, and surfactants are a problem, they may be extracted using the following procedure. Acidify the sample with acetic acid (1.6M) to pH 6.0 to 7.0.

CAUTION: This procedure can produce lethal HCN gas.

Extract with isooctane, hexane, or chloroform (preference in order named) with solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the compounds below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is completed, immediately raise the pH of the sample to above 12 with 50% NaOH solution.

7.0 PROCEDURE

7.1 Pretreatment for cyanides amenable to chlorination

7.1.1 This test must be performed under amber light. $K_3[Fe(CN)_6]$ may decompose under UV light and hence will test positive for cyanide amenable to chlorination if exposed to fluorescent lighting or sunlight. Two identical sample aliquots are required to determine cyanides amenable to chlorination.

7.1.2 To one 500 mL sample or to a sample diluted to 500 mL, add calcium hypochlorite solution dropwise while agitating and maintaining the pH between 11 and 12 with 1.25N sodium hydroxide until an excess of chlorine is present as indicated by KI-starch paper turning blue. The sample will be subjected to alkaline chlorination by this step.

CAUTION: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is necessary that this reaction be performed in a hood.

7.1.3 Test for excess chlorine with KI-starch paper and maintain this excess for one hour with continuous agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional calcium hypochlorite solution.

7.1.4 After one hour, add 1 mL portions of 0.1N sodium arsenite until KI-starch paper shows no residual chlorine. Add 5 mL of excess sodium arsenite to ensure the presence of excess reducing agent.

7.1.5 Test for total cyanide as described below in both the chlorinated and the unchlorinated samples. The difference of total cyanide in the chlorinated and unchlorinated samples is the cyanide amenable to chlorination.

7.2 Distillation Procedure

7.2.1 Place 500 mL of sample, or sample diluted to 500 mL in the one liter boiling flask. Pipet 50 mL of 1.25N sodium hydroxide into the gas scrubber. If the apparatus in Figure 1 is used, add water until the spiral is covered. Connect the boiling flask, condenser, gas scrubber and vacuum trap.

7.2.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately two bubbles of air per second enter the boiling flask through the air inlet tube.

7.2.3 If samples are known or suspected to contain sulfide, add 50 mL of 0.062M bismuth nitrate solution through the air inlet tube. Mix for three minutes. Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper.

7.2.4 If samples are known or suspected to contain nitrate or nitrite, or if bismuth nitrate was added to the sample, add 50 mL of 0.4N sulfamic acid solution through the air inlet tube. Mix for three minutes.

Note: Excessive use of sulfamic acid could create method bias.

7.2.5 Slowly add 50 mL of 18N sulfuric acid through the air inlet tube. Rinse the tube with water and allow the airflow to mix the flask contents for three minutes. Add 20 mL of 2.5M magnesium chloride through the air inlet and wash the inlet tube with a stream of water.

7.2.6 Heat the solution to boiling. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, and closing the vacuum source, disconnect the gas scrubber.

7.2.7 Transfer the solution from the scrubber into a 250-mL volumetric flask. Rinse the scrubber into the volumetric flask. Dilute to volume with water.

7.2.8 If the manual spectrophotometric determination will be performed, proceed to Step 7.3.1. If the titration procedure will be performed, proceed to Step 7.7.

7.3 Manual spectrophotometric determination

7.3.1 Pipet 50 mL of the scrubber solution into a 100-mL volumetric flask. If the sample is later found to be beyond the linear range of the colorimetric determination and redistillation of a smaller sample is not feasible, a smaller aliquot may be taken. If less than 50 mL is taken, dilute to 50 mL with 0.25N sodium hydroxide solution.

NOTE: Temperature of reagents and spiking solution can affect the response factor of the colorimetric determination. The reagents stored in the refrigerator should be warmed to ambient temperature before use. Samples should not be left in a warm instrument to develop color, but instead they should be aliquoted to a cuvette immediately prior to reading the absorbance.

7.3.2 Add 15 mL of 1M sodium phosphate solution and mix. Add 2 mL of chloramine-T and mix. Some distillates may contain compounds that have chlorine demand. One minute after the addition of chloramine-T, test for excess chlorine with KI-starch paper. If the test is negative, add 0.5 mL chloramine-T. After one minute recheck with KI-starch paper. Continue to add chloramine-T in 0.5 mL increments until an excess is maintained. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution and mix.

7.3.3 Dilute to 100 mL with water and mix again. Allow 8 minutes for color development and then read the absorbance at 578 nm in a 1-cm cell within 15 minutes. The sodium hydroxide concentration will be 0.125N.

7.4 Standard curve for samples without sulfide

7.4.1 Prepare a series of standards by pipetting suitable volumes of working standard potassium cyanide solution into 250-mL volumetric flasks. To each flask, add 50 mL of 1.25N sodium hydroxide and dilute to 250 mL with water. Prepare using the following table. The sodium hydroxide concentration will be 0.25N.

mL of Working Standard Solution (1 mL = 10 µg CN^-)	Concentration (µg CN^-/L)
0	Blank
1.0	40
2.0	80
5.0	200
10.0	400
15.0	600
20.0	800

7.4.2 After the standard solutions have been prepared according to the table above, pipet 50 mL of each standard solution into a 100-mL volumetric flask and proceed to Steps 7.3.2 and 7.3.3 to obtain absorbance values for the standard curve. The final concentrations for the standard curve will be one half of the amounts in the above table (final concentrations ranging from 20 to 400 µg/L).

7.4.3 It is recommended that at least two standards (a high and a low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within ± 10% of the undistilled standards, the analyst should find the cause of the apparent error before proceeding.

7.4.4 Prepare a standard curve ranging from 20 to 400 µg/L by plotting absorbance of standard versus the cyanide concentration

7.5 Standard curve for samples with sulfide

7.5.1 It is imperative that all standards be distilled in the same manner as the samples using the method of standard additions. Standards distilled by this method will give a linear curve, at low concentrations, but as the concentration increases, the recovery decreases. It is recommended that at least five standards be distilled.

7.5.2 Prepare a series of standards similar in concentration to those mentioned in Step 7.4.1 and analyze as in Step 7.3. Prepare a standard curve by plotting absorbance of standard versus the cyanide concentration.

7.6 Calculation - If the spectrophotometric procedure is used, calculate the cyanide, in µg/L, in the original sample as follows.

$$CN^- \ (\mu g/L) = \frac{A \times B \times C}{D \times E}$$

where:

A = $\mu g/L$ CN^- read from standard curve.
B = mL of sample after preparation of colorimetric analysis (100 mL recommended).
C = mL of sample after distillation (250 mL recommended).
D = mL of original sample for distillation (500 mL recommended).
E = mL used for colorimetric analysis (50 mL recommended).

7.7 Titration Procedure

7.7.1 Transfer the gas scrubber solution or a suitable aliquot from the 250-mL volumetric flask to a 500-mL Erlenmeyer flask. Add 10-12 drops of the rhodanine indicator.

7.7.2 Titrate with standard 0.0192N silver nitrate to the first change in color from yellow to brownish-pink. The titration must be performed slowly with constant stirring. Titrate a water blank using the same amount of sodium hydroxide and indicator as in the sample. The analyst should be familiar with the endpoint of the titration and the amount of indicator to be used before actually titrating the samples. A 5-mL buret may be conveniently used to obtain a precise titration.

NOTE: The titration is based on the following reaction:

$$Ag^+ + 2CN \rightarrow [Ag(CN)_2]^-$$

When all of the cyanide has complexed and more silver nitrate is added, the excess silver combines with the rhodanine indicator to turn the solution yellow and then brownish-pink.

7.7.3 Calculation - If the titrimetric procedure is used, calculate concentration of CN^- in $\mu g/L$ in the original sample as follows:

$$CN^-(\mu g/L) = \frac{(A-B)}{C} \times D \times \frac{E}{F} \times \frac{2\ mole\ CN^-}{1\ eq.\ AgNO_3} \times \frac{26.02\ g\ CN^-}{1\ mole\ CN^-} \times \frac{1 \times 10^6 \mu g}{1\ g}$$

where:

A = mL of $AgNO_3$ for titration of sample.
B = mL of $AgNO_3$ for titration of blank.
C = mL of sample titrated (250 recommended).
D = actual normality of $AgNO_3$ (0.0192N recommended).
E = mL of sample after distillation (250 recommended).
F = mL of original sample before distillation (500 recommended).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one reagent blank per analytical batch or one in every 20 samples to determine if contamination or any memory effects are occurring.

8.3 Analyze check standards with every analytical batch of samples. If the standards are not within 15% of the expected value, then the samples must be reanalyzed.

8.4 Run one replicate sample for every 20 samples. A replicate sample is a sample brought through the entire sample preparation and analytical process. The CV of the replicates should be 20% or less. If this criterion is not met, the samples should be reanalyzed.

8.5 Run one matrix spiked sample every 20 samples to check the efficiency of sample distillation by adding cyanide from the working standard or intermediate standard to 500 mL of sample to ensure a concentration of approximately 40 μg/L. The matrix spiked sample is brought through the entire sample preparation and analytical process.

8.6 The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences such as samples which contain sulfides.

9.0 METHOD PERFORMANCE

9.1 The titration procedure using silver nitrate is used for measuring concentrations of cyanide exceeding 0.1 mg/L. The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

9.2 EPA Method 335.2 (sample distillation with titration) reports that in a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.06 to 0.62 mg/L CN^-, the standard deviations for precision were $\pm$ 0.005 to $\pm$ 0.094, respectively. In a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/L CN^-, recoveries (accuracy) were 85% and 102%, respectively.

9.3 In two additional studies using surface water, ground water, and landfill leachate samples, the titration procedure was further evaluated. The concentration range used in these studies was 0.5 to 10 mg/L cyanide. The detection limit was found to be 0.2 mg/L for both total and amenable cyanide determinations. The precision (CV) was 6.9 and 2.6 for total cyanide determinations and 18.6 and 9.1 for amenable cyanide determinations. The mean recoveries were 94% and 98.9% for total cyanide, and 86.7% and 97.4% for amenable cyanide.

10.0 REFERENCES

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FIGURE 1.
APPARATUS FOR CYANIDE DISTILLATION

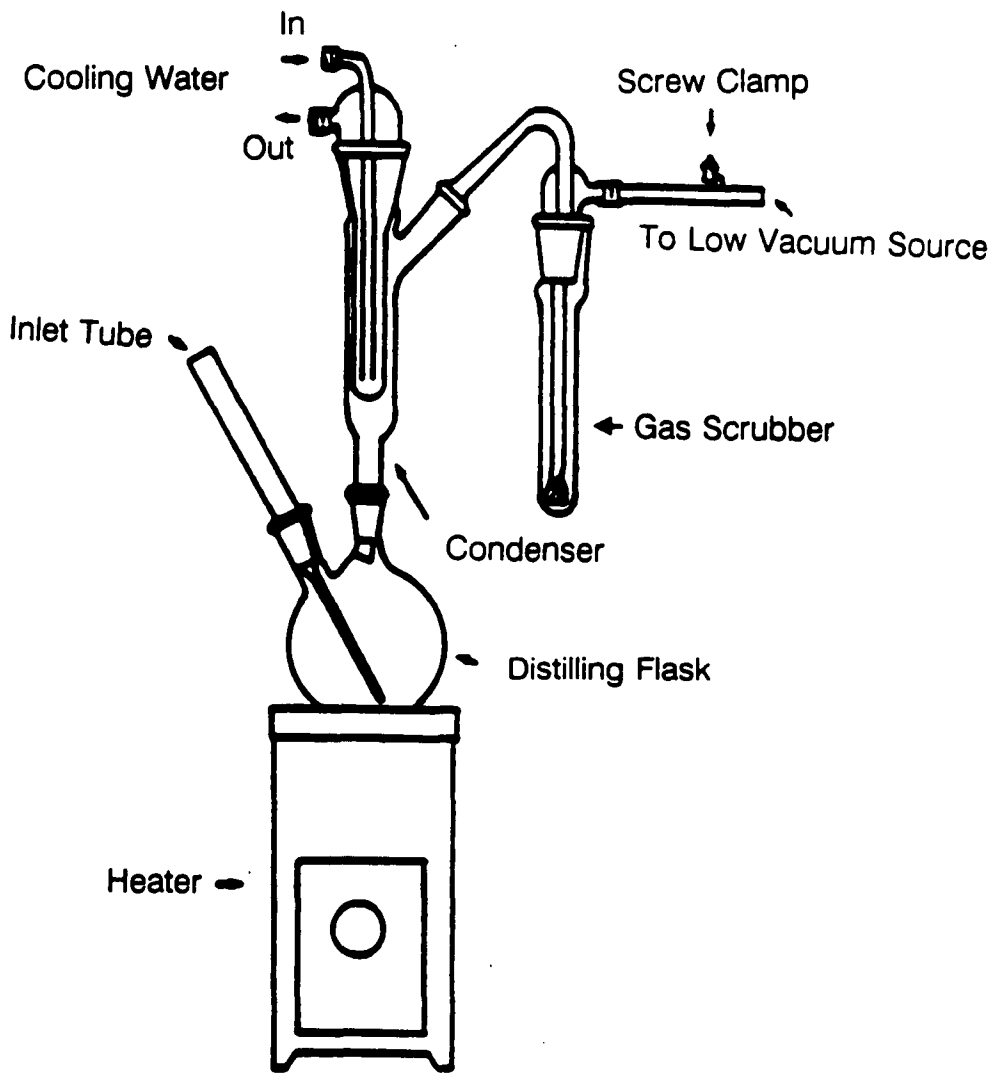
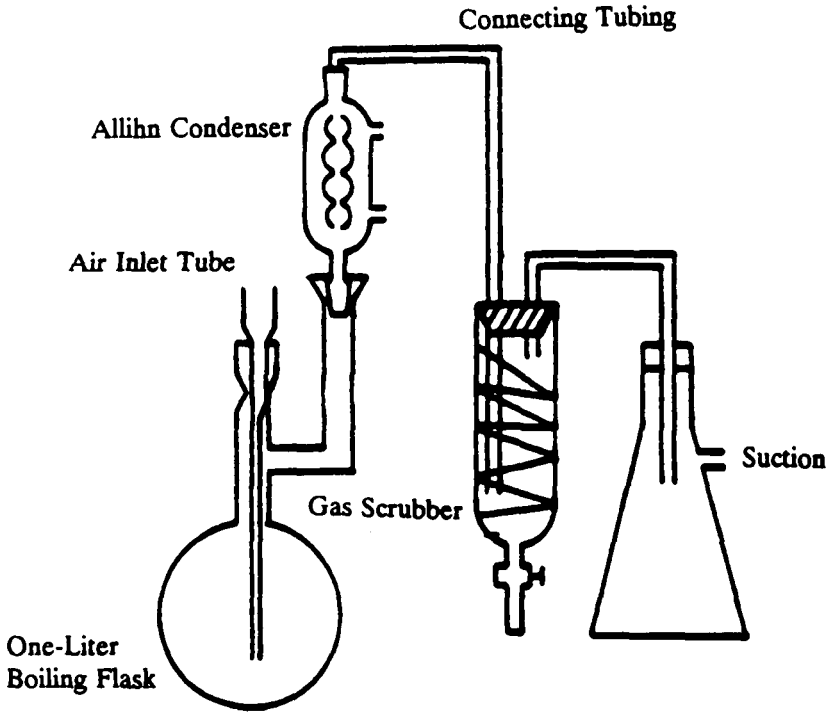
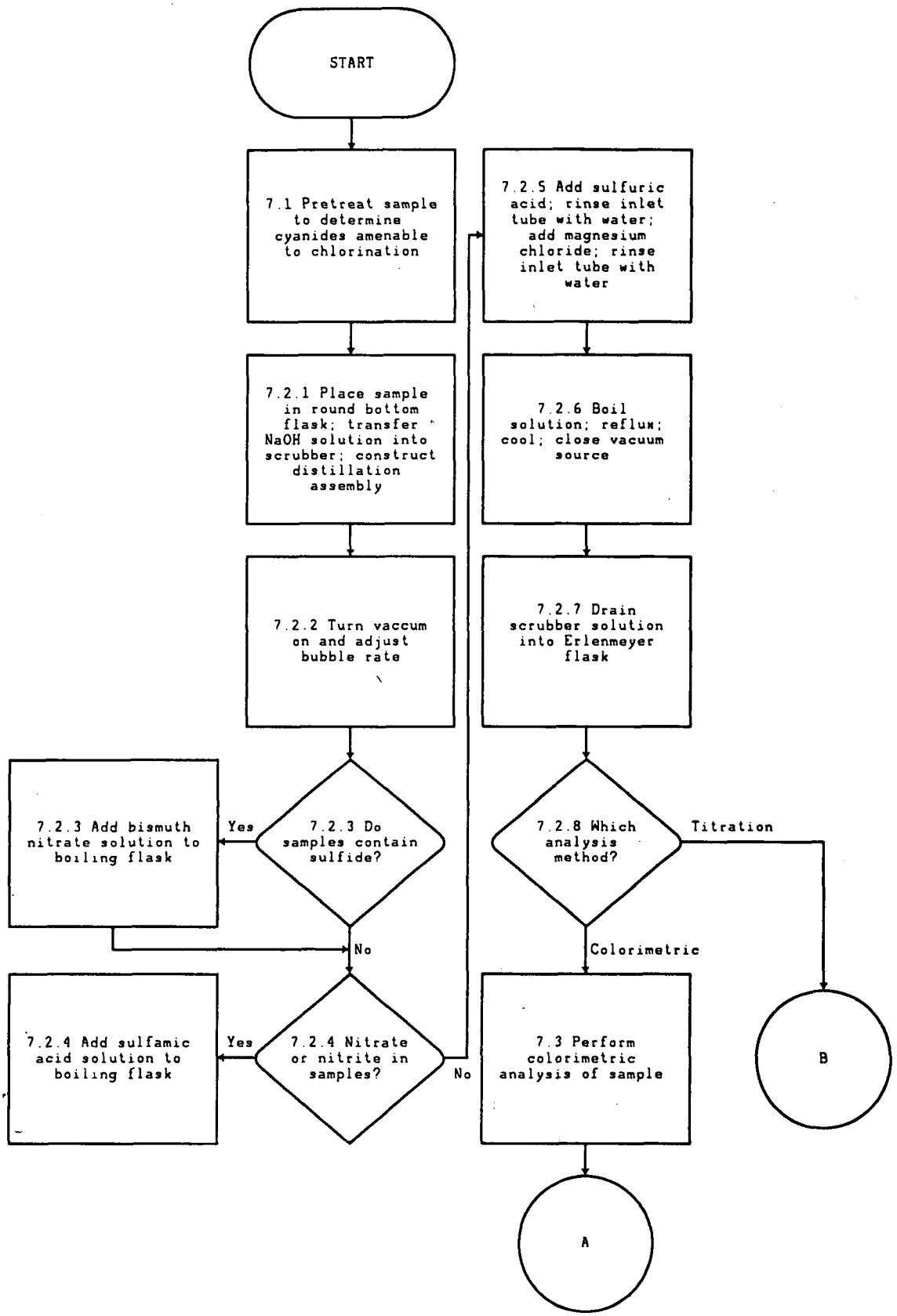
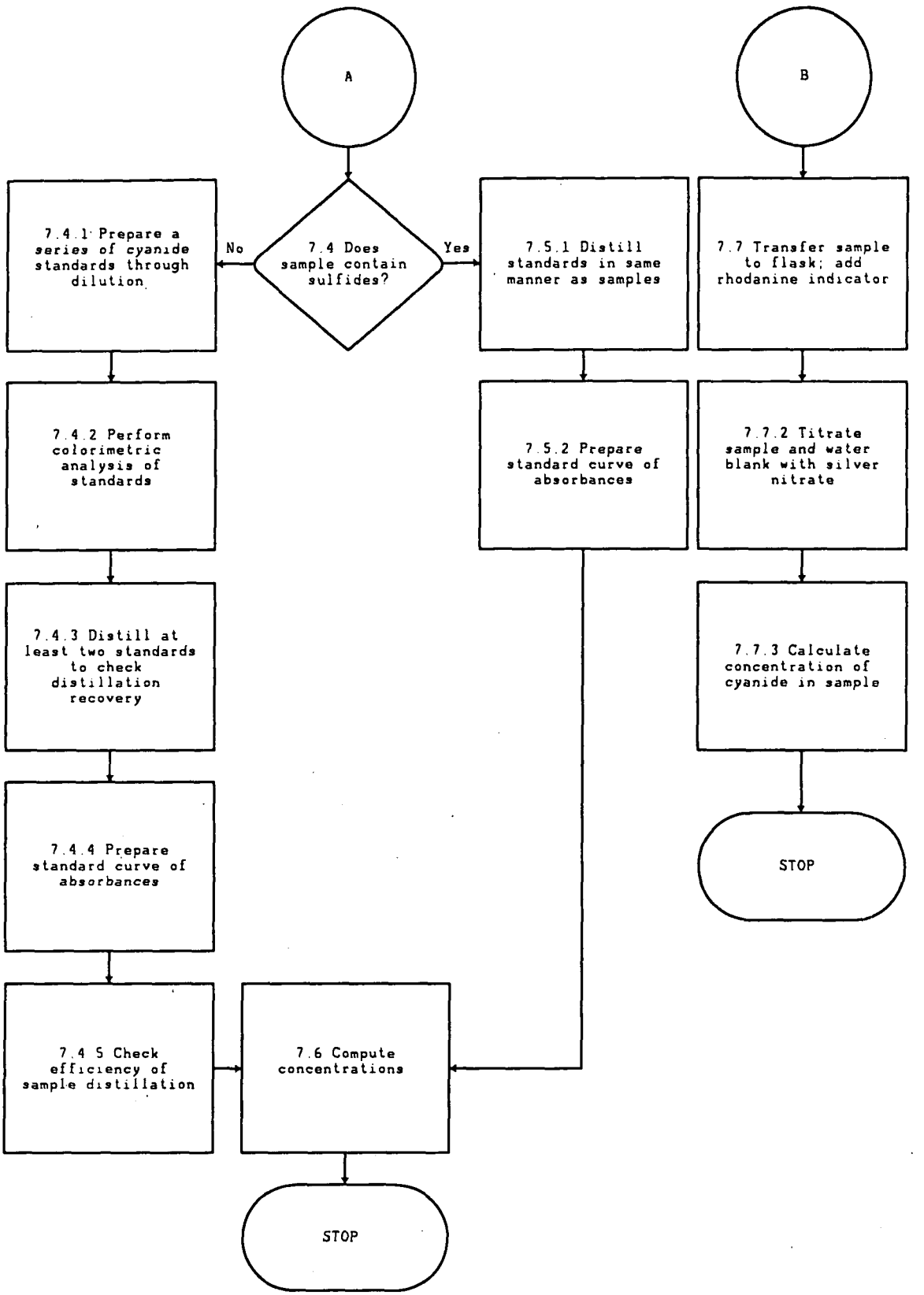


FIGURE 2.
APPARATUS FOR CYANIDE DISTILLATION



TOTAL AND AMENABLE CYANIDE




A
B
7.4.1 Prepare a series of cyanide standards through dilution
No
7.4 Does sample contain sulfides?
Yes
7.5.1 Distill standards in same manner as samples
7.7 Transfer sample to flask; add rhodanine indicator
7.4.2 Perform colorimetric analysis of standards
7.5.2 Prepare standard curve of absorbances
7.7.2 Titrate sample and water blank with silver nitrate
7.4.3 Distill at least two standards to check distillation recovery
7.7.3 Calculate concentration of cyanide in sample
7.4.4 Prepare standard curve of absorbances
STOP
7.4.5 Check efficiency of sample distillation
7.6 Compute concentrations
STOP

METHOD 9012

TOTAL AND AMENABLE CYANIDE (COLORIMETRIC, AUTOMATED UV)

1.0 SCOPE AND APPLICATION

1.1 Method 9012 is used to determine the concentration of inorganic cyanide in an aqueous waste or leachate. The method detects inorganic cyanides that are present as either simple soluble salts or complex radicals. It is used to determine values for both total cyanide and cyanide amenable to chlorination. Method 9012 is not intended to determine if a waste is hazardous by the characteristic of reactivity.

2.0 SUMMARY OF METHOD

2.1 The cyanide, as hydrocyanic acid (HCN), is released by refluxing the sample with strong acid and distillation of the HCN into an absorber-scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by automated UV colorimetry.

2.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction with Chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The concentration of NaOH must be the same in the standards, the scrubber solutions, and any dilution of the original scrubber solution to obtain colors of comparable intensity.

3.0 INTERFERENCES

3.1 Interferences are eliminated or reduced by procedures described in Paragraphs 7.2.3, 7.2.4, and 7.2.5.

3.2 Sulfides adversely affect the colorimetric procedures. Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during the distillation should be treated by addition of bismuth nitrate prior to distillation as described in Paragraph 7.2.3.

3.3 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds will decompose under test conditions to generate HCN. The possible interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid.

4.0 APPARATUS AND MATERIALS

4.1 Reflux distillation apparatus: Such as shown in Figure 1 or 2. The boiling flask should be of 1-liter size with inlet tube and provision for condenser. The gas absorber is a Fisher-Milligan scrubber (Fisher Catalog #07-513) or equivalent.

4.2 Potassium iodide-starch test paper.

4.3 Automated continuous-flow analytical instrument with:

4.3.1 Sampler.
4.3.2 Manifold with UV digestor.
4.3.3 Proportioning pump.
4.3.4 Heating bath with distillation coil.
4.3.5 Distillation head.
4.3.6 Colorimeter equipped with a 15-mm flowcell and 570 nm filter.
4.3.7 Recorder.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Sodium hydroxide solution, 1.25 N: Dissolve 50 g of NaOH in Type II water and dilute to 1 liter with Type II water.

5.3 Bismuth nitrate solution: Dissolve 30.0 g of $Bi(NO_3)_3$ in 100 mL of Type II water. While stirring, add 250 mL of glacial acetic acid. Stir until dissolved. Dilute to 1 liter with Type II water.

5.4 Sulfuric acid, 1:1: Slowly add 500 mL of concentrated H_2SO_4 to 500 mL of Type II water.
CAUTION: this is an exothermic reaction.

5.5 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in 1 liter of Type II water.

5.6 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 900 mL of Type II water. Standardize with 0.0192 N $AgNO_3$. Dilute to appropriate concentration so that 1 mL = 1 mg CN.

5.7 Intermediate standard cyanide solution: Dilute 100.0 mL of stock (1 mL = 1 mg CN) to 1,000 mL with Type II water (1 mL = 100 ug CN).

5.8 Working standard cyanide solution: Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1,000 mL with Type II water (1 mL = 10.0 ug CN). Store in a glass-stoppered bottle.

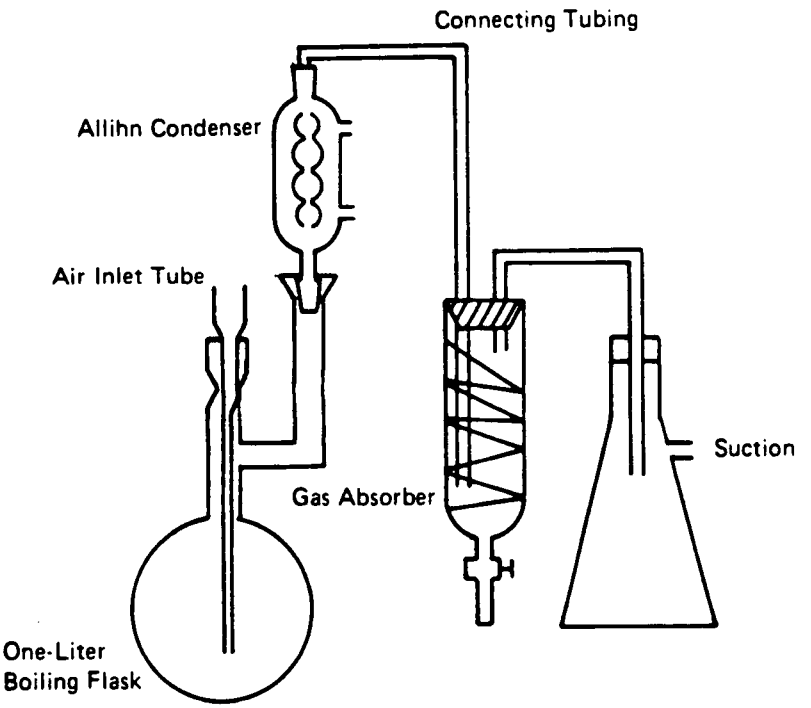


Figure 1. Apparatus for cyanide distillation.

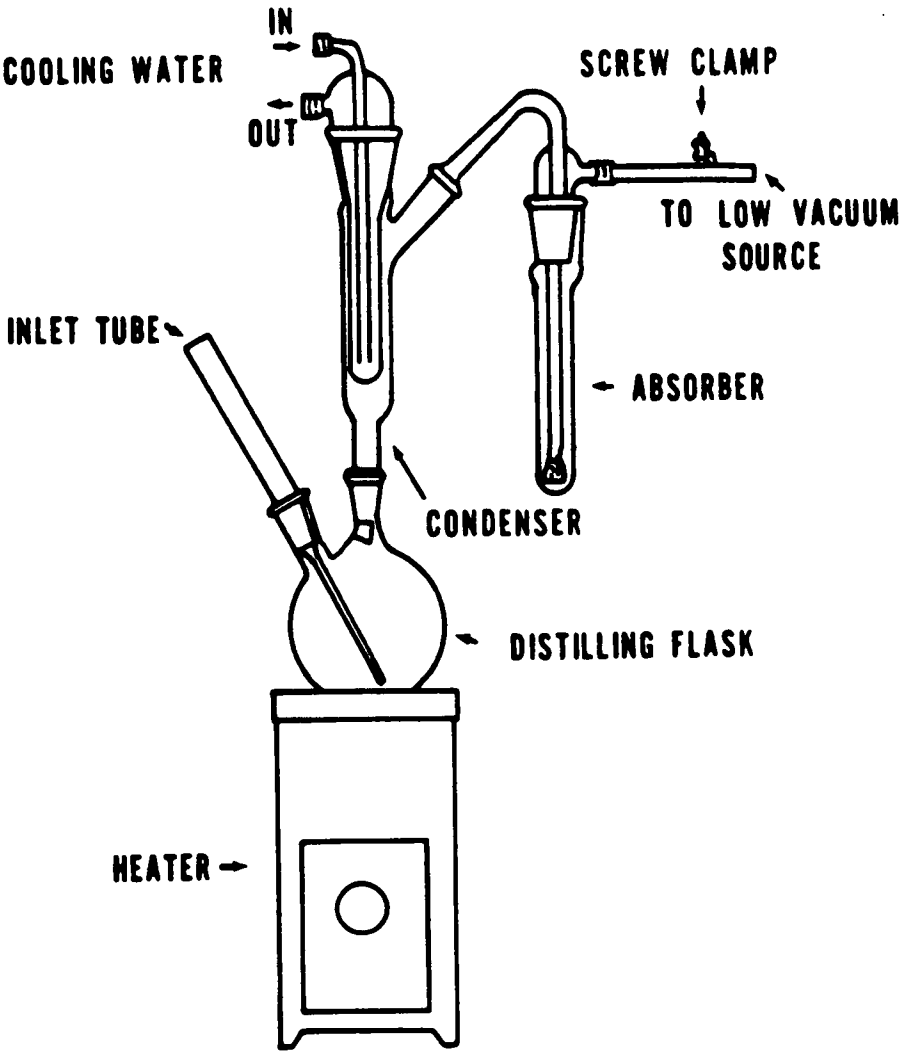


Figure 2. Cyanide distillation apparatus.

5.9 Magnesium chloride solution: Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1,000-mL flask, dissolve, and dilute to 1 liter with Type II water.

5.10 Sulfamic acid solution: Dissolve 40 g of sulfamic acid in Type II water. Dilute to 1 liter.

5.11 Calcium hypochlorite solution: Dissolve 5 g of calcium hypochlorite [$Ca(OCl)_2$] in 100 mL of Type II water.

5.12 Reagents for automated colorimetric determination:

5.12.1 **Pyridine-barbituric acid reagent:** Place 15 g of barbituric acid in a 250-mL volumetric flask, add just enough Type II water to wash the sides of the flask, and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of concentrated HCl, mix, and cool to room temperature. Dilute to 250 mL with Type II water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

5.12.2 **Chloramine-T solution:** Dissolve 2.0 g of white, water soluble chloramine-T in 500 mL of Type II water and refrigerate until ready to use.

5.12.3 **Sodium hydroxide, 1 N:** Dissolve 40 g of NaOH in Type II water, and dilute to 1 liter.

5.12.4 All working standards should contain 2 mL of 1 N NaOH (Paragraph 5.12.3) per 100 mL.

5.12.5 **Dilution water and receptacle wash water** (NaOH, 0.25 N): Dissolve 10.0 g NaOH in 500 mL of Type II water. Dilute to 1 liter.

5.13 Ascorbic acid: Crystals.

5.14 Phosphate buffer, pH 5.2: Dissolve 13.6 g of potassium dihydrogen phosphate and 0.28 g of disodium phosphate in 900 mL of Type II water and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples should be collected in plastic or glass bottles of 1-liter size or larger. All bottles must be thoroughly cleaned and thoroughly rinsed to remove soluble materials from containers.

6.3 Oxidizing agents such as chlorine decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with acidified potassium iodide (KI)-starch test paper at the time the sample is collected; a blue color indicates the need for treatment. Add ascorbic acid a

few crystals at a time until a drop of sample produces no color on the indicator. Then add an additional 0.6 g of ascorbic acid for each liter of water.

6.4 Samples must be preserved by addition of 10 N sodium hydroxide until sample pH is greater than or equal to 12 at the time of collection.

6.5 Samples should be refrigerated at 4°C, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Pretreatment for cyanides amenable to chlorination:

7.1.1 Two sample aliquots are required to determine cyanides amenable to chlorination. To one 500-mL aliquot, or to a volume diluted to 500 mL, add calcium hypochlorite solution (Paragraph 5.11) dropwise while agitating and maintaining the pH between 11 and 12 with sodium hydroxide (Paragraph 5.2).

CAUTION: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is recommended that this reaction be performed in a hood. For convenience, the sample may be agitated in a 1-liter beaker by means of a magnetic stirring device.

7.1.2 Test for residual chlorine with KI-starch paper (Paragraph 4.4) and maintain this excess for 1 hr, continuing agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional hypochlorite solution.

7.1.3 After 1 hr, add 0.5 g portions of ascorbic acid until KI-starch paper shows no residual chlorine. Add an additional 0.5 g of ascorbic acid to ensure the presence of excess reducing agent.

7.1.4 Test for total cyanide in both the chlorinated and unchlorinated aliquots. (The difference of total cyanide in the chlorinated and unchlorinated aliquots is the cyanide amenable to chlorination.)

7.2 Distillation Procedure:

7.2.1 Place 500 mL of sample, or an aliquot diluted to 500 mL, in the 1-liter boiling flask. Pipet 50 mL of sodium hydroxide (Paragraph 5.2) into the absorbing tube. If the apparatus in Figure 1 is used, add Type II water until the spiral is covered. Connect the boiling flask, condenser, absorber, and trap in the train (Figure 1 or 2).

7.2.2 By adjusting the vacuum source, start a slow stream of air entering the boiling flask so that approximately two bubbles of air per second enter the flask through the air inlet tube.

7.2.3 Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper. If positive, treat the sample by adding 50 mL of bismuth nitrate solution (Paragraph 5.3) through the air inlet tube after the air rate is set. Mix for 3 min prior to addition of H_2SO_4.

7.2.4 If samples are suspected to contain NO_3 and/or NO_2, add 50 mL of sulfamic acid solution (Paragraph 5.10) after the air rate is set through the air inlet tube. Mix for 3 min prior to addition of H_2SO_4.

7.2.5 Slowly add 50 mL 1:1 H_2SO_4 (Paragraph 5.4) through the air inlet tube. Rinse the tube with Type II water and allow the airflow to mix the flask contents for 3 min. Pour 20 mL of magnesium chloride (Paragraph 5.9) into the air inlet and wash down with a stream of water.

7.2.6 Heat the solution to boiling. Reflux for 1 hr. Turn off heat and continue the airflow for at least 15 min. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

7.2.7 Drain the solution from the absorber into a 250-mL volumetric flask. Wash the absorber with Type II water and add the washings to the flask. Dilute to the mark with Type II water.

7.3 Automated colorimetric determination:

7.3.1 Set up the manifold in a hood or a well-ventilated area as shown in Figure 3.

7.3.2 Allow colorimeter and recorder to warm up for 30 min. Run a baseline with all reagents, feeding Type II water through the sample line.

7.3.3 Place appropriate standards in the sampler in order of decreasing concentration. Complete loading of the sampler tray with unknown samples.

7.3.4 When the baseline becomes steady, begin the analysis.

7.4 Standard curve for samples without sulfide:

7.4.1 Prepare a series of standards by pipetting suitable volumes of standard solution (Paragraph 5.8) into 250-mL volumetric flasks. To each standard add 50 mL of 1.25 N sodium hydroxide and dilute to 250 mL with Type II water. Prepare as follows:

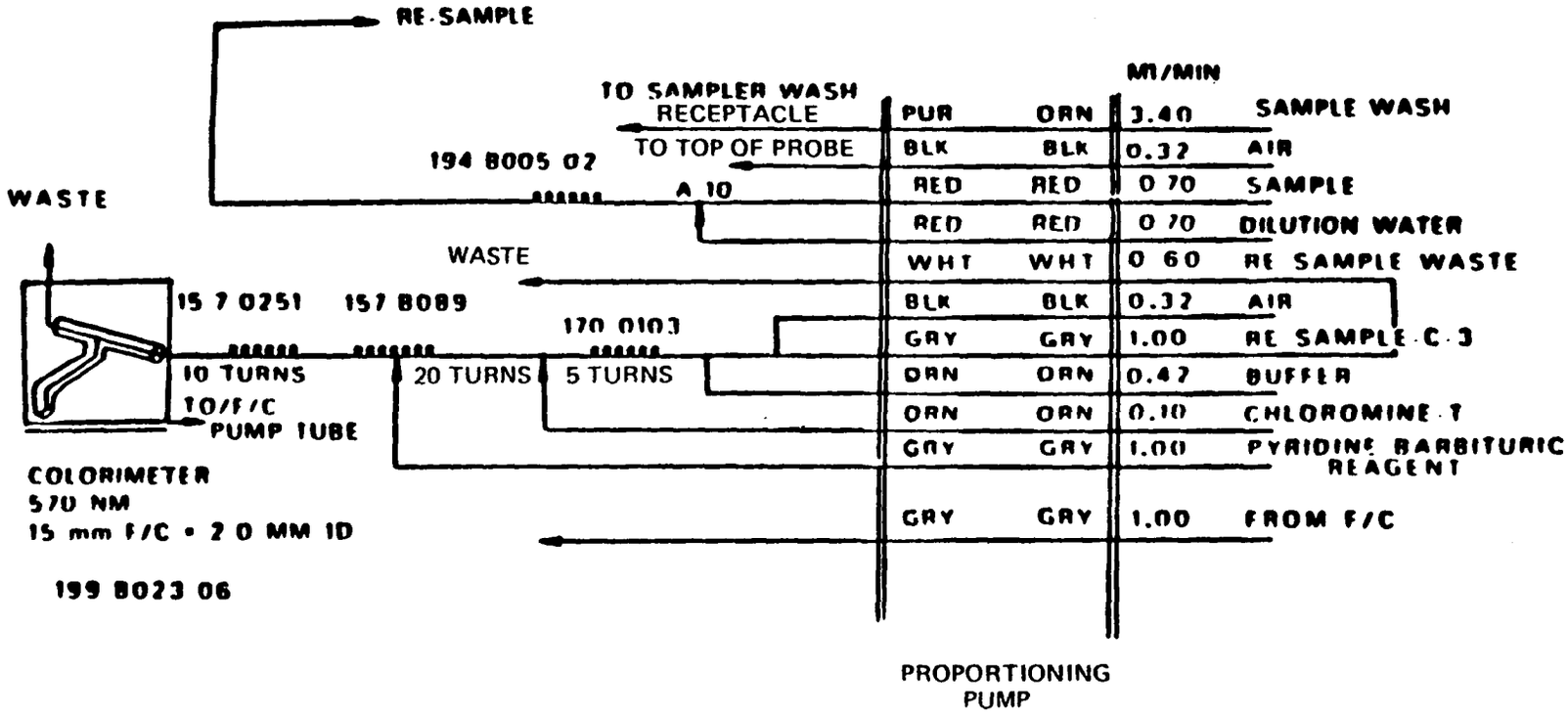


Figure 3. Cyanide manifold AA11.

mL of Working Standard Solution (1 mL = 10 ug CN)	Concentration (ug CN/250 mL)
0	BLANK
1.0	10
2.0	20
5.0	50
10.0	100
15.0	150
20.0	200

7.4.2 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and a low) be distilled and compared with similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within ± 10% of the undistilled standards, the analyst should find the cause of the apparent error before proceeding.

7.4.3 Prepare a standard curve by plotting absorbances of standards vs. cyanide concentrations.

7.4.4 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (Paragraph 5.7) or the working standard (Paragraph 5.8) to 500 mL of sample to ensure a level of 20 ug/L. Proceed with the analysis as in Paragraph 7.2.1.

7.5 Standard curve for samples with sulfide:

7.5.1 All standards must be distilled in the same manner as the samples. A minimum of 3 standards shall be distilled.

7.5.2 Prepare a standard curve by plotting absorbances of standards vs. cyanide concentration.

7.6 Calculation: Prepare a standard curve by plotting peak heights of standards against their concentration values. Compute concentrations of samples by comparing sample peak heights with the standard curve.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 Verify calibration with an independently prepared check standard every 15 samples.

8.4 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.5 The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are not available at this time.

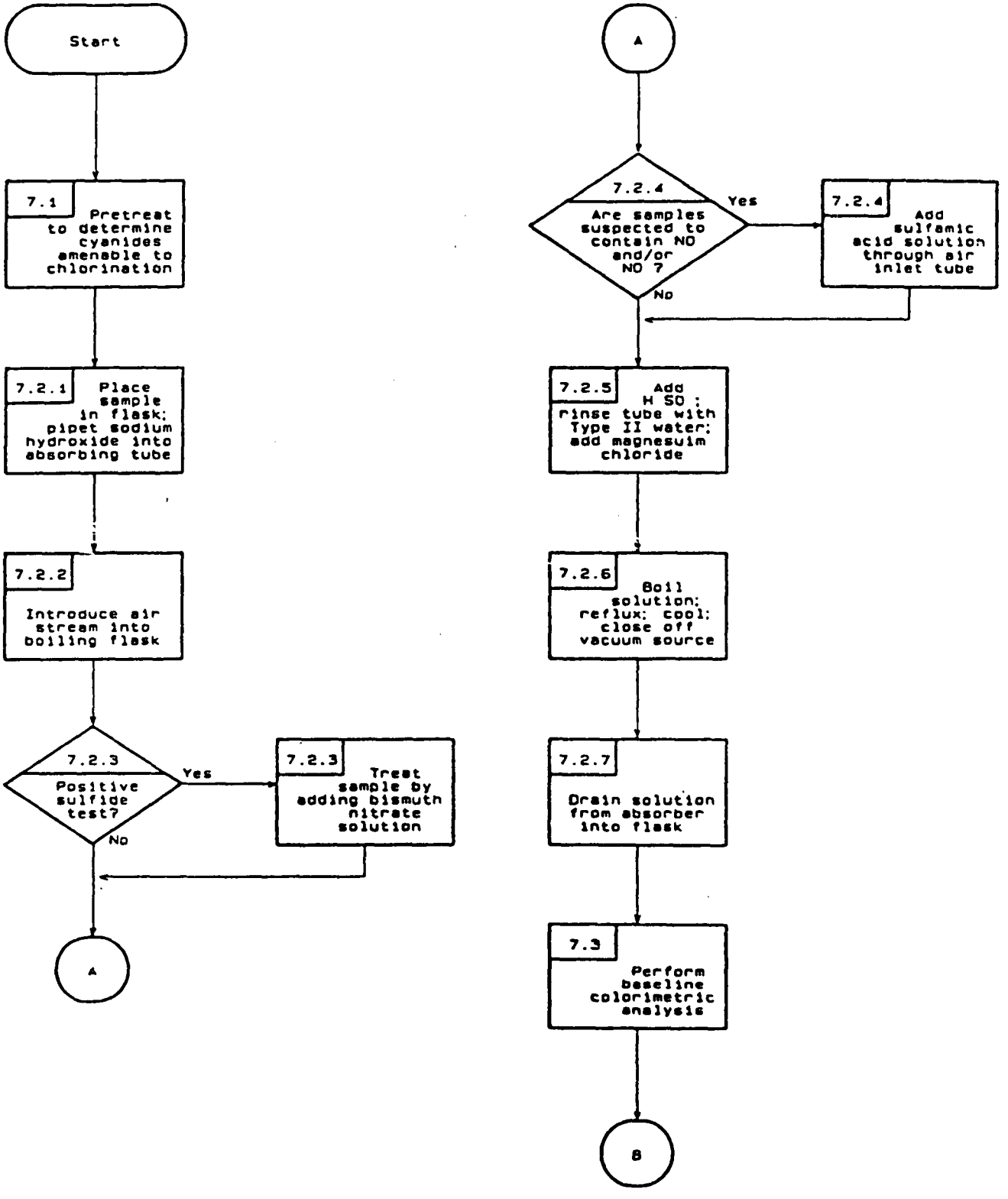
10.0 REFERENCES

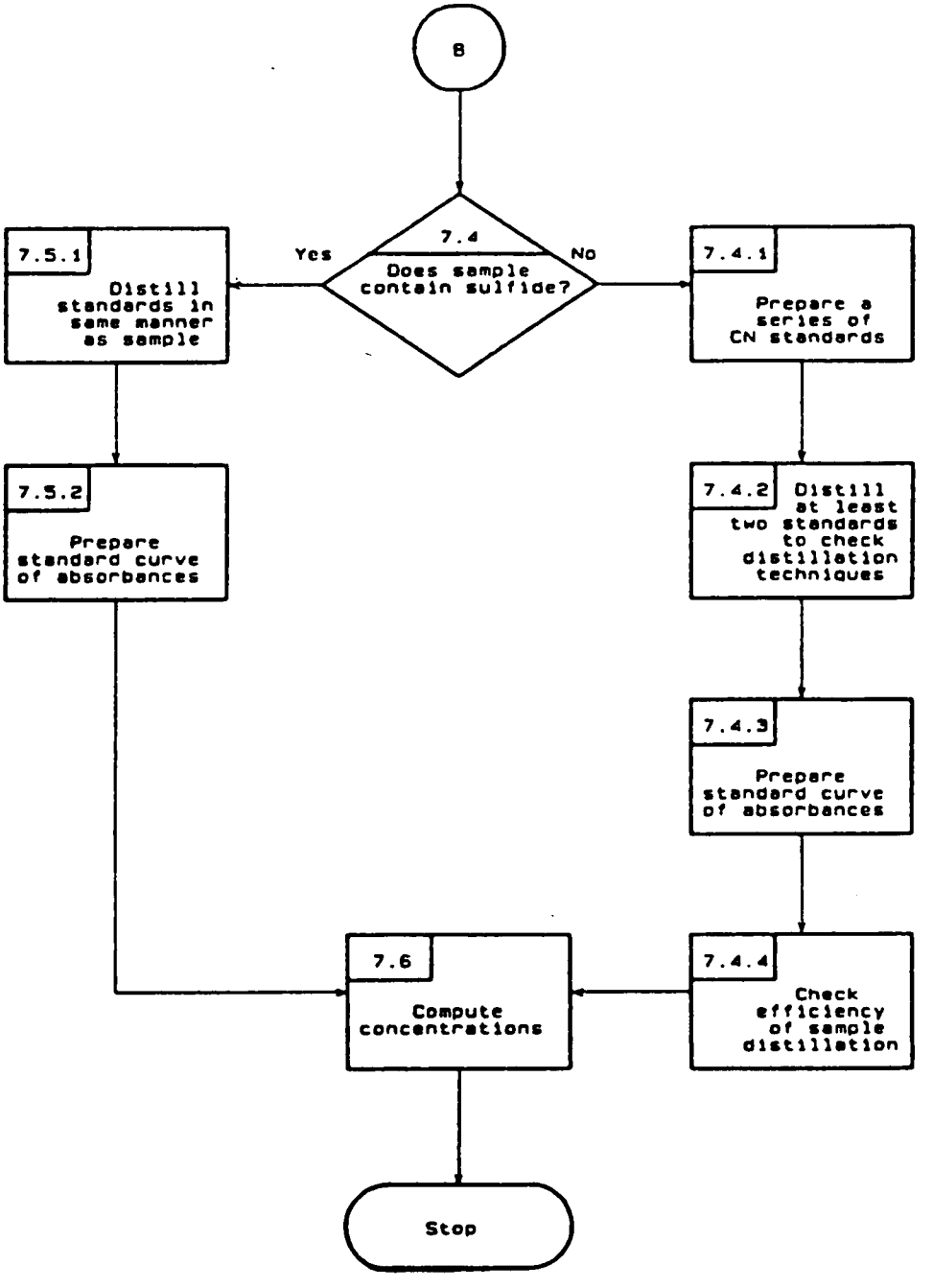
1. Annual Book of ASTM Standards, Part 31, "Water," Standard D2036-75, Method B, p. 505 (1976).

2. Goulden, P.D., B.K. Afghan, and P. Brooksbank, Determination of Nanogram Quantities of Simple and Complex Cyanides in Water, Anal. Chem., 44(11), pp. 1845-49 (1972).

3. Standard Methods for the Examination of Water and Wastewater, 14th ed., pp. 376 and 370, Method 413F and D (1975).

4. Technicon AutoAnalyzer II Methodology, Industrial Method No. 315-74 WCUV Digestion and Distillation, Technicon Industrial Systems, Tarrytown, New York, 10591 (1974).


Start
7.1
Pretreat to determine cyanides amenable to chlorination
7.2.1
Place sample in flask; pipet sodium hydroxide into absorbing tube
7.2.2
Introduce air stream into boiling flask
7.2.3
Positive sulfide test?
Yes
No
7.2.3
Treat sample by adding bismuth nitrate solution
A
A
7.2.4
Are samples suspected to contain NO and/or NO 7
Yes
No
7.2.4
Add sulfamic acid solution through air inlet tube
7.2.5
Add H SO ; rinse tube with Type II water; add magnesuim chloride
7.2.6
Boil solution; reflux; cool; close off vacuum source
7.2.7
Drain solution from absorber into flask
7.3
Perform baseline colorimetric analysis
B


8
7.4
Does sample contain sulfide?
Yes
No
7.5.1
Distill standards in same manner as sample
7.5.2
Prepare standard curve of absorbances
7.4.1
Prepare a series of CN standards
7.4.2
Distill at least two standards to check distillation techniques
7.4.3
Prepare standard curve of absorbances
7.4.4
Check efficiency of sample distillation
7.6
Compute concentrations
Stop

METHOD 9013
(APPENDIX TO METHOD 9010)

CYANIDE EXTRACTION PROCEDURE FOR SOLIDS AND OILS

1.0 SCOPE AND APPLICATION

1.1 The extraction procedure described in this method is designed for the extraction of soluble cyanides from solid and oil wastes. The method is applicable to oil, solid, and multiphasic samples. This method is not applicable to samples containing insoluble cyanide compounds.

2.0 SUMMARY OF METHOD

2.1 If the waste sample contains so much solid, or solids of such a size as to interfere with agitation and homogenization of the sample mixture in the distillation flask, or so much oil or grease as to interfere with the formation of a homogeneous emulsion, the sample may be extracted with water at pH 10 or greater, and the extract distilled and analyzed by Method 9010. Samples that contain free water are filtered and separated into an aqueous component and a combined oil and solid component. The nonaqueous component may then be extracted, and an aliquot of the extract combined with an aliquot of the filtrate in proportion to the composition of the sample. Alternatively, the components may be analyzed separately, and cyanide levels reported for each component. However, if the sample solids are known to contain sufficient levels of cyanide (about 50 μg/g) as to be well above the limit of detection, the extraction step may be deleted and the solids analyzed directly by Method 9010. This can be accomplished by diluting a small aliquot of the waste solid (1-10 g) in 500 mL water in the distillation flask and suspending the slurry during distillation with a magnetic stir-bar.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in Method 9010.

4.0 APPARATUS AND MATERIALS

4.1 Extractor - Any suitable device that sufficiently agitates a sealed container of one liter volume or greater. For the purpose of this analysis, agitation is sufficient when:

1. All sample surfaces are continuously brought into contact with extraction fluid, and

2. The agitation prevents stratification of the sample and fluid.

4.2 Buchner funnel apparatus

4.2.1 Buchner funnel - 500-mL capacity, with 1-liter vacuum filtration flask.

4.2.2 Glass wool - Suitable for filtering, 0.8 m diameter such as Corning Pyrex 3950.

4.2.3 Vacuum source - Preferably a water driven aspirator. A valve or stopcock to release vacuum is required.

4.3 Top-loading balance - capable of weighing 0.1 g.

4.4 Separatory funnels - 500 mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Sodium hydroxide (50% w/v), NaOH. Commercially available.

5.4 n-Hexane, C_6H_{14}.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a plan that addresses the considerations discussed in Chapter 4 of this manual. See Section 6.0 of Method 9010 for additional guidance.

7.0 PROCEDURE

7.1 If the waste does not contain any free aqueous phase, go to Step 7.5. If the sample is a homogeneous fluid or slurry that does not separate or settle in the distillation flask when using a Teflon coated magnetic stirring bar but mixes so that the solids are entirely suspended, then the sample may be analyzed by Method 9010 without an extraction step.

7.2 Assemble Buchner funnel apparatus. Unroll glass filtering fiber and fold the fiber over itself several times to make a pad about 1 cm thick when lightly compressed. Cut the pad to fit the Buchner funnel. Weigh the pad, then place it in the funnel. Turn the aspirator on and wet the pad with a known amount of water.

7.3 Transfer the sample to the Buchner funnel in small aliquots, first decanting the fluid. Rinse the sample container with known amounts of water and add the rinses to the Buchner funnel. When no free water remains in the funnel, slowly open the stopcock to allow air to enter the vacuum flask. A small amount of sediment may have passed through the glass fiber pad. This will not interfere with the analysis.

7.4 Transfer the solid and the glass fiber pad to a tared weighing dish. Since most greases and oils will not pass through the fiber pad, solids, oils, and greases will be extracted together. If the filtrate includes an oil phase, transfer the filtrate to a separatory funnel. Collect and measure the volume of the aqueous phase. Transfer the oil phase to the weighing dish with the solid.

7.5 Weigh the dish containing solid, oil (if any), and filter pad. Subtract the weight of the dry filter pad. Calculate the net volume of water present in the original sample by subtracting the total volume of rinses used from the measured volume of the filtrate.

7.6 Place the following in a 1-liter wide-mouthed bottle:

500 mL water
5 mL 50% w/v NaOH
50 mL n-Hexane (if a heavy grease is present)

If the weight of the solids (Step 7.5) is greater than 25 g, weigh out a representative aliquot of 25 g and add it to the bottle; otherwise add all of the solids. Cap the bottle.

7.7 The pH of the extract must be maintained above 10 throughout the extraction step and subsequent filtration. Since some samples may release acid, the pH must be monitored as follows. Shake the extraction bottle and after one minute, check the pH. If the pH is below 12, add 50% NaOH in 5 mL increments until it is at least 12. Recap the bottle, and repeat the procedure until the pH does not drop.

7.8 Place the bottle or bottles in the tumbler, making sure there is enough foam insulation to cushion the bottle. Turn the tumbler on and allow the extraction to run for about 16 hours.

7.9 Prepare a Buchner funnel apparatus as in Step 7.2 with a glass fiber pad filter.

7.10 Decant the extract to the Buchner funnel. Full recovery of the extract is not necessary.

7.11 If the extract contains an oil phase, separate the aqueous phase using a separatory funnel. Neither the separation nor the filtration are critical, but are necessary to be able to measure the volume of the aliquot of the aqueous extract analyzed. Small amounts of suspended solids and oil emulsions will not interfere.

7.12 At this point, an aliquot of the filtrate of the original sample may be combined with an aliquot of the extract in a proportion representative of the sample. Alternatively, they may be distilled and analyzed separately and concentrations given for each phase. This is described by the following equation:

$$\frac{\text{Liquid Sample Aliquot(mL)}}{\text{Extract Aliquot(mL)}} = \frac{\text{Solid Extracted(g)}^{a}}{\text{Total Solid(g)}^{b}} \times \frac{\text{Total Sample Filtrate(mL)}^{c}}{\text{Total Extraction Fluid(mL)}^{d}}$$

[a]From Step 7.6. Weight of solid sample used for extraction.

[b]From Step 7.5. Weight of solids and oil phase with the dry weight of filter and tared dish subtracted.

[c]Includes volume of all rinses added to the filtrate (Steps 7.2 and 7.3).

[d]500 mL water plus total volume of NaOH solution. Does not include hexane, which is subsequently removed (Step 7.11).

Alternatively, the aliquots may be distilled and analyzed separately, concentrations for each phase reported separately, and the amounts of each phase present in the sample reported separately.

8.0 QUALITY CONTROL

8.1 Refer to Method 9010.

9.0 METHOD PERFORMANCE

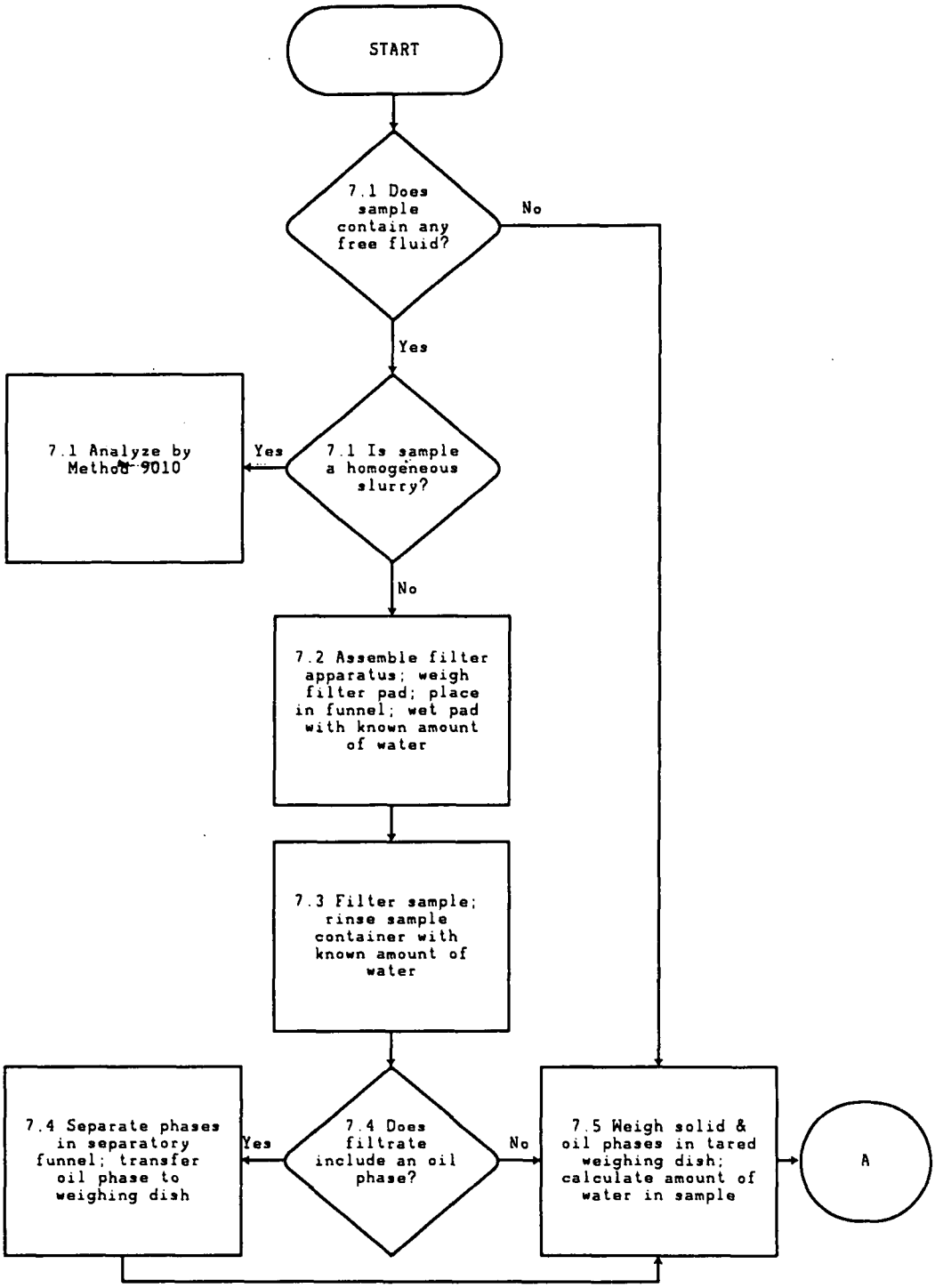
9.1 In a single laboratory study, recoveries of 60 to 90% are reported for solids and 88 to 92% for oils. The reported CVs are less than 13.

10.0 REFERENCES

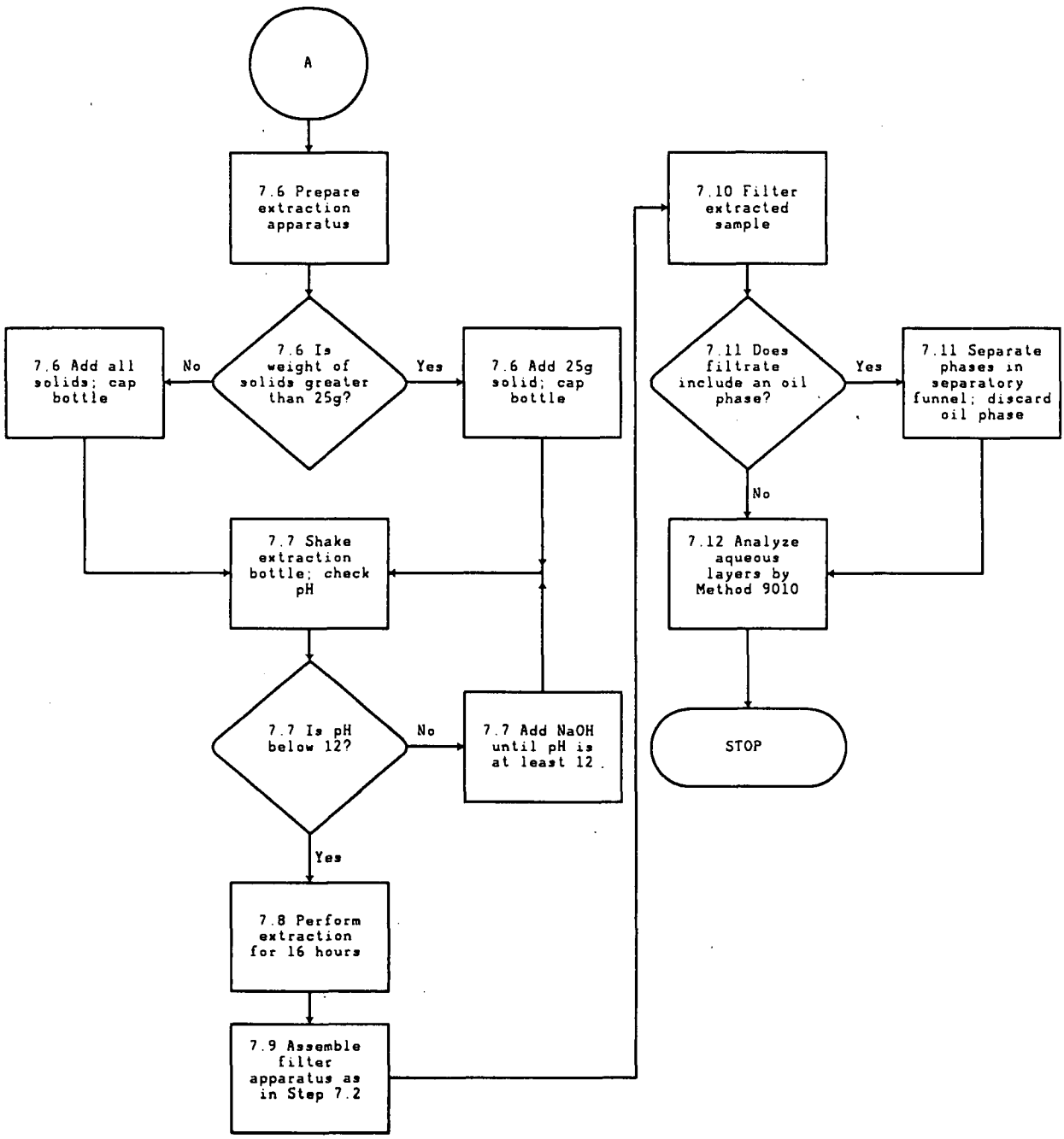
10.1 Refer to Method 9010.

METHOD 9013
(APPENDIX TO METHOD 9010)

CYANIDE EXTRACTION PROCEDURE FOR SOLIDS AND OILS



CYANIDE EXTRACTION PROCEDURE FOR SOLIDS AND OILS (CONTINUED)



METHOD 9020B

TOTAL ORGANIC HALIDES (TOX)

1.0 SCOPE AND APPLICATION

1.1 Method 9020 determines Total Organic Halides (TOX) as chloride in drinking water and ground waters. The method uses carbon adsorption with a microcoulometric-titration detector.

1.2 Method 9020 detects all organic halides containing chlorine, bromine, and iodine that are adsorbed by granular activated carbon under the conditions of the method. Fluorine-containing species are not determined by this method.

1.3 Method 9020 is applicable to samples whose inorganic-halide concentration does not exceed the organic-halide concentration by more than 20,000 times.

1.4 Method 9020 does not measure TOX of compounds adsorbed to undissolved solids.

1.5 Method 9020 is restricted to use by, or under the supervision of, analysts experienced in the operation of a pyrolysis/microcoulometer and in the interpretation of the results.

1.6 This method is provided as a recommended procedure. It may be used as a reference for comparing the suitability of other methods thought to be appropriate for measurement of TOX (i.e., by comparison of sensitivity, accuracy, and precision of data).

2.0 SUMMARY OF METHOD

2.1 A sample of water that has been protected against the loss of volatiles by the elimination of headspace in the sampling container, and that is free of undissolved solids, is passed through a column containing 40 mg of activated carbon. The column is washed to remove any trapped inorganic halides and is then combusted to convert the adsorbed organohalides to HX, which is trapped and titrated electrolytically using a microcoulometric detector.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample-processing hardware. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by treating with chromate cleaning solution. This should be followed by detergent washing in hot water. Rinse with tap water and distilled water and drain dry; glassware which is not volumetric should, in addition, be heated in a muffle furnace at 400°C for 15 to 30 min. (Volumetric ware should not be heated in a muffle

furnace.) Glassware should be sealed and stored in a clean environment after drying and cooling to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high-purity reagents and gases helps to minimize interference problems.

3.2 Purity of the activated carbon must be verified before use. Only carbon samples that register less than 1,000 ng Cl^-/40 mg should be used. The stock of activated carbon should be stored in its granular form in a glass container with a Teflon seal. Exposure to the air must be minimized, especially during and after milling and sieving the activated carbon. No more than a 2-wk supply should be prepared in advance. Protect carbon at all times from all sources of halogenated organic vapors. Store prepared carbon and packed columns in glass containers with Teflon seals.

3.3 Particulate matter will prevent the passage of the sample through the adsorption column. Particulates must, therefore, be eliminated from the sample. This must be done as gently as possible, with the least possible sample manipulation, in order to minimize the loss of volatiles. It should also be noted that the measured TOX will be biased by the exclusion of TOX from compounds adsorbed onto the particulates. The following techniques may be used to remove particulates; however, data users must be informed of the techniques used and their possible effects on the data. These techniques are listed in order of preference:

3.3.1 Allow the particulates to settle in the sample container and decant the supernatant liquid into the adsorption system.

3.3.2 Centrifuge sample and decant the supernatant liquid into the adsorption system.

3.3.3 Measure Purgeable Organic Halides (POX) of sample (see SW-846 Method 9021) and Non-Purgeable Organic Halides (NPOX, that is, TOX of sample that has been purged of volatiles) separately, where the NPOX sample is centrifuged or filtered.

4.0 APPARATUS AND MATERIALS

4.1 Adsorption system (a schematic diagram of the adsorption system is shown in Figure 1):

4.1.1 Adsorption module: Pressurized sample and nitrate-wash reservoirs.

4.1.2 Adsorption columns: Pyrex, 5-cm-long x 6-mm-O.D. x 2-mm-I.D.

4.1.3 Granular activated carbon (GAC): Filtrasorb-400, Calgon-APC or equivalent, ground or milled, and screened to a 100/200 mesh range. Upon combustion of 40 mg of GAC, the apparent halide background should be 1,000 ng Cl^- equivalent or less.

4.1.4 Cerafelt (available from Johns-Manville) or equivalent: Form this material into plugs to fit the adsorption module and to hold 40 mg of GAC in the adsorption columns.

CAUTION: Do not touch this material with your fingers. Oily residue will contaminate carbon.

4.1.5 Column holders.

4.1.6 Class A volumetric flasks: 100-mL and 50-mL.

4.2 Analytical system:

4.2.1 Microcoulometric-titration system: Containing the following components (a flowchart of the analytical system is shown in Figure 2):

4.2.1.1 Boat sampler: Muffled at 800°C for at least 2-4 min and cleaned of any residue by vacuuming after each run.

4.2.1.2 Pyrolysis furnace.

4.2.1.3 Microcoulometer with integrator.

4.2.1.4 Titration cell.

4.2.2 Recording device.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Sodium sulfite (0.1 M), Na_2SO_3: Dissolve 12.6 g ACS reagent grade Na_2SO_3 in reagent water and dilute to 1 L.

5.4 Concentrated nitric acid (HNO_3).

5.5 Nitrate-wash solution (5,000 mg NO_3^-/L), KNO_3: Prepare a nitrate-wash solution by transferring approximately 8.2 g of potassium nitrate (KNO_3) into a 1-liter Class A volumetric flask and diluting to volume with reagent water.

5.6 Carbon dioxide (CO_2): Gas, 99.9% purity.

5.7 Oxygen (O_2): 99.9% purity.

5.8 Nitrogen (N_2): Prepurified.

5.9 Acetic acid in water (70%), $C_2H_4O_2$: Dilute 7 volumes of glacial acetic acid with 3 volumes of reagent water.

5.10 Trichlorophenol solution, stock (1 μL = 10 μg Cl^-): Prepare a stock solution by accurately weighing accurately 1.856 g of trichlorophenol into a 100-mL Class A volumetric flask. Dilute to volume with methanol.

5.11 Trichlorophenol solution, calibration (1 μL = 500 ng Cl^-), $C_6H_3Cl_3O$: Dilute 5 mL of the trichlorophenol stock solution to 100 mL with methanol.

5.12 Trichlorophenol standard, instrument calibration: First, nitrate-wash a single column packed with 40 mg of activated carbon, as instructed for sample analysis, and then inject the column with 10 μL of the calibration solution.

5.13 Trichlorophenol standard, adsorption efficiency (100 μg Cl^-/liter): Prepare an adsorption-efficiency standard by injecting 10 μL of stock solution into 1 liter of reagent water.

5.14 Blank standard: The methanol used to prepare the calibration standard should be used as the blank standard.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 All samples should be collected in bottles with Teflon septa (e.g., Pierce #12722 or equivalent) and be protected from light. If this is not possible, use amber glass 250-mL bottles fitted with Teflon-lined caps. Foil may be substituted for Teflon if the sample is not corrosive. Samples must be preserved by acidification to pH <2 with sulfuric acid, stored at 4°C, and protected against loss of volatiles by eliminating headspace in the container. Samples should be analyzed within 28 days. The container must be washed and muffled at 400°C before use, to minimize contamination.

6.3 All glassware must be dried prior to use according to the method discussed in Sec. 3.1.1.

7.0 PROCEDURE

7.1 Sample preparation:

7.1.1 Special care should be taken in handling the sample in order to minimize the loss of volatile organohalides. The adsorption procedure should be performed simultaneously on duplicates.

7.1.2 Reduce residual chlorine by adding sulfite (5 mg sodium sulfite crystals per liter of sample). Sulfite should be added at the time of sampling if the analysis is meant to determine the TOX concentration at the time of sampling. It should be recognized that TOX

may increase on storage of the sample. Samples should be stored at 4°C without headspace.

7.2 Calibration:

7.2.1 Check the adsorption efficiency of each newly prepared batch of carbon by analyzing 100 mL of the adsorption efficiency standard, in duplicate, along with duplicates of the blank standard. The net recovery should be within 10% of the standard value.

7.2.2 Nitrate-wash blanks (method blanks): Establish the repeatability of the method background each day by first analyzing several nitrate-wash blanks. Monitor this background by spacing nitrate-wash blanks between each group of ten pyrolysis determinations. The nitrate-wash blank values are obtained on single columns packed with40 mg of activated carbon. Wash with the nitrate solution, as instructed for sample analysis, and then pyrolyze the carbon.

7.2.3 Pyrolyze duplicate instrument-calibration standards and the blank standard each day before beginning sample analysis. The net response to the calibration standard should be within 10% of the calibration-standard value. Repeat analysis of the instrument-calibration standard after each group of ten pyrolysis determinations and before resuming sample analysis, and after cleaning or reconditioning the titration cell or pyrolysis system.

7.3 Adsorption procedure:

7.3.1 Connect two columns in series, each containing 40 mg of 100/200-mesh activated carbon.

7.3.2 Fill the sample reservoir and pass a metered amount of sample through the activated-carbon columns at a rate of approximately 3 mL/min.

NOTE: 100 mL of sample is the preferred volume for concentrations of TOX between 5 and 500 µg/L, 50 mL for 501 to 1000 µg/L, and 25 mL for 1001 to 2000 µg/L. If the anticipated TOX is greater than 2000 µg/L, dilute the sample so that 100 mL will contain between 1 and 50 µg TOX.

7.3.3 Wash the columns-in-series with 2 mL of the 5,000-mg/L nitrate solution at a rate of approximately 2 mL/min to displace inorganic chloride ions.

7.4 Pyrolysis procedure:

7.4.1 The contents of each column are pyrolyzed separately. After being rinsed with the nitrate solution, the columns should be protected from the atmosphere and other sources of contamination until ready for further analysis.

7.4.2 Pyrolysis of the sample is accomplished in two stages. The volatile components are pyrolyzed in a CO_2-rich atmosphere at a low temperature to ensure the conversion of brominated trihalomethanes to a titratable species. The less volatile components are then pyrolyzed at a high temperature in an O_2-rich atmosphere.

7.4.3 Transfer the contents of each column to the quartz boat for individual analysis.

7.4.4 Adjust gas flow according to manufacturer's directions.

7.4.5 Position the sample for 2 min in the 200°C zone of the pyrolysis tube.

7.4.6 After 2 min, advance the boat into the 800°C zone (center) of the pyrolysis furnace. This second and final stage of pyrolysis may require from 6 to 10 min to complete.

7.5 Detection: The effluent gases are directly analyzed in the micro-coulometric-titration cell. Carefully follow manual instructions for optimizing cell performance.

7.6 Breakthrough: The unpredictable nature of the background bias makes it especially difficult to recognize the extent of breakthrough of organohalides from one column to another. All second-column measurements for a properly operating system should not exceed 10% of the two-column total measurement. If the 10% figure is exceeded, one of three events could have happened: (1) the first column was overloaded and a legitimate measure of breakthrough was obtained, in which case taking a smaller sample may be necessary; (2) channeling or some other failure occurred, in which case the sample may need to be rerun; or (3) a high random bias occurred, and the result should be rejected and the sample rerun. Because it may not be possible to determine which event occurred, a sample analysis should be repeated often enough to gain confidence in results. As a general rule, any analysis that is rejected should be repeated whenever a sample is available. In the event that repeated analyses show that the second column consistently exceeds the 10% figure and the total is too low for the first column to be saturated and the inorganic Cl is less than 20,000 times the organic chlorine value, then the result should be reported, but the data user should be informed of the problem. If the second-column measurement is equal to or less than the nitrate-wash blank value, the second-column value should be disregarded.

7.7 Calculations: TOX as Cl^- is calculated using the following formula:

$$\frac{(C_1 - C_3) + (C_2 - C_3)}{V} = \mu g/L \text{ Total Organic Halide}$$

where:

C_1 = μg Cl^- on the first column in series;

C_2 = μg Cl^- on the second column in series;

C_3 = predetermined, daily, average, method-blank value (nitrate-wash blank for a 40-mg carbon column); and

V = the sample volume in liters.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control guidelines.

8.2 This method requires that all samples be run in duplicate.

8.3 Employ a minimum of two blanks to establish the repeatability of the method background, and monitor the background by spacing method blanks between each group of eight analytical determinations.

8.4 After calibration, verify it with an independently prepared check standard.

8.5 Run matrix spike between every 10 samples and bring it through the entire sample preparation and analytical process.

9.0 METHOD PERFORMANCE

9.1 Under conditions of duplicate analysis, the method detection limit is 10 μg/L.

9.2 Analyses of distilled water, uncontaminated ground water, and ground water from RCRA waste management facilities spiked with volatile chlorinated organics generally gave recoveries between 75-100% over the concentration range 10-500 μg/L. Relative standard deviations were generally 20% at concentrations greater than 25 μg/L. These data are shown in Tables 1 and 2.

10.0 REFERENCES

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TABLE 1. METHOD PERFORMANCE DATA[a]

Spiked Compound	Matrix[b]	TOX Concentration (μg/L)	Percent Recovery
Bromobenzene	D.W.	443	95
Bromodichloromethane	D.W	160	98
Bromoform	D.W.	160	110
Bromoform	D.W.	238	100
Bromoform	G.W.	10	140
Bromoform	G.W.	31	93
Bromoform	G.W.	100	120
Chloroform	D.W.	98	89
Chloroform	D.W.	112	94
Chloroform	G.W.	10	79
Chloroform	G.W.	30	76
Chloroform	G.W.	100	81
Dibromodichloromethane	D.W.	155	86
Dibromodichloromethane	D.W.	374	73
Tetrachloroethylene	G.W.	10	79
Tetrachloroethylene	G.W.	30	75
Tetrachloroethylene	G.W.	101	78
trans-Dichloroethylene	G.W.	10	84
trans-Dichloroethylene	G.W.	30	63
trans-Dichloroethylene	G.W.	98	60

[a]Results from Reference 2.

[b]G.W. = Ground Water.
D.W. = Distilled Water.

TABLE 2. METHOD PERFORMANCE DATA[a]

Sample Matrix	Unspiked TOX Levels (μg/L)	Spike Level	Percent Recoveries
Ground Water	68, 69	100	98, 99
Ground Water	5, 12	100	110, 110
Ground Water	5, 10	100	95, 105
Ground Water	54, 37	100	111, 106
Ground Water	17, 15	100	98, 89
Ground Water	11, 21	100	97, 89

[a]Results from Reference 3.

Fig. 1. Schematic Diagram of Adsorption System

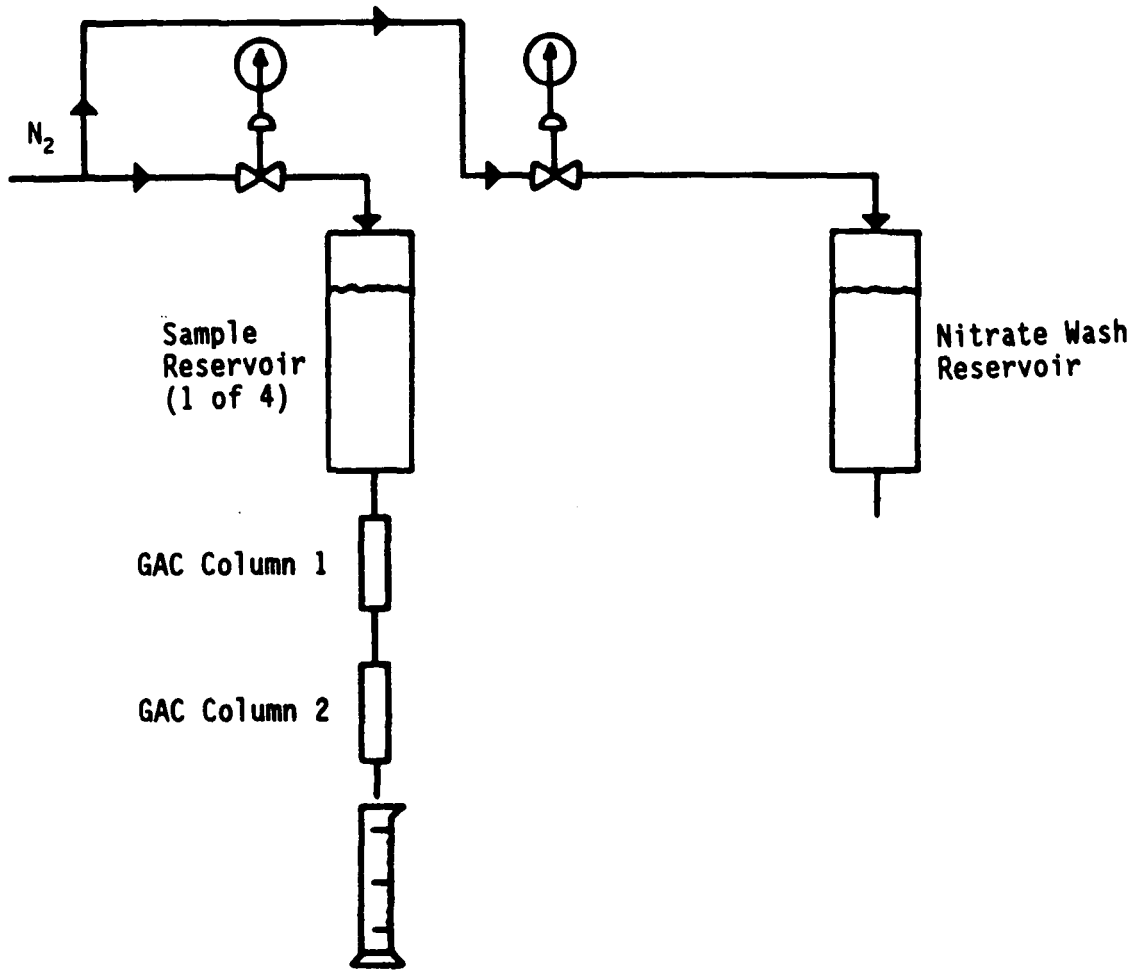
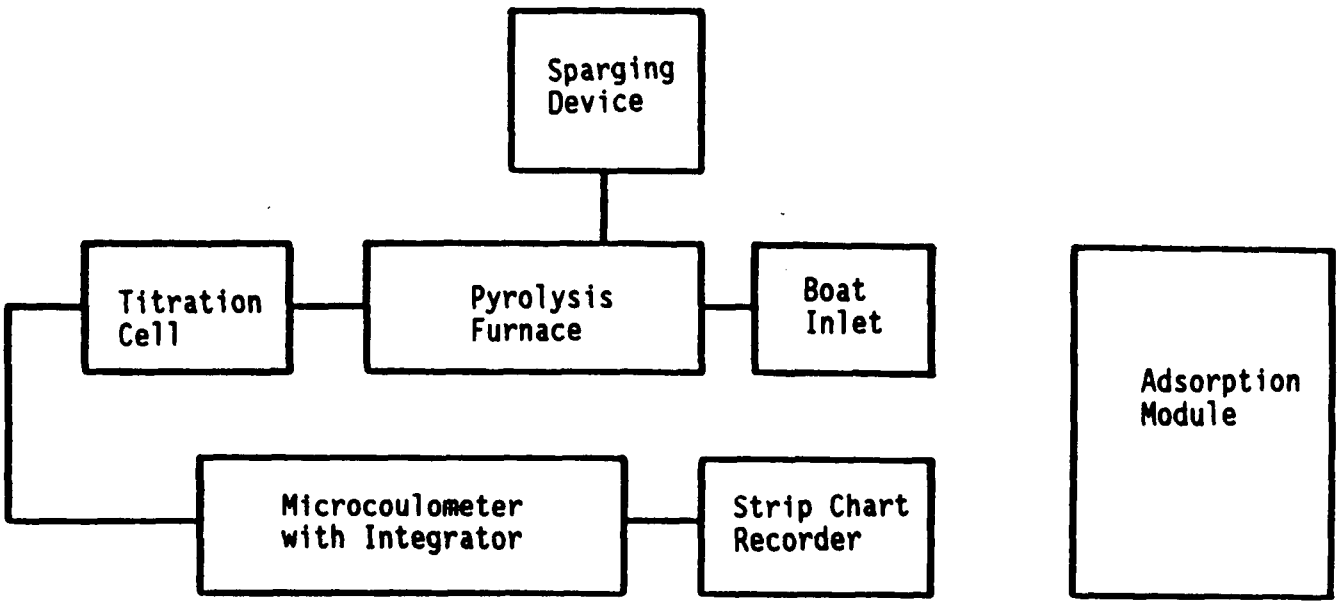
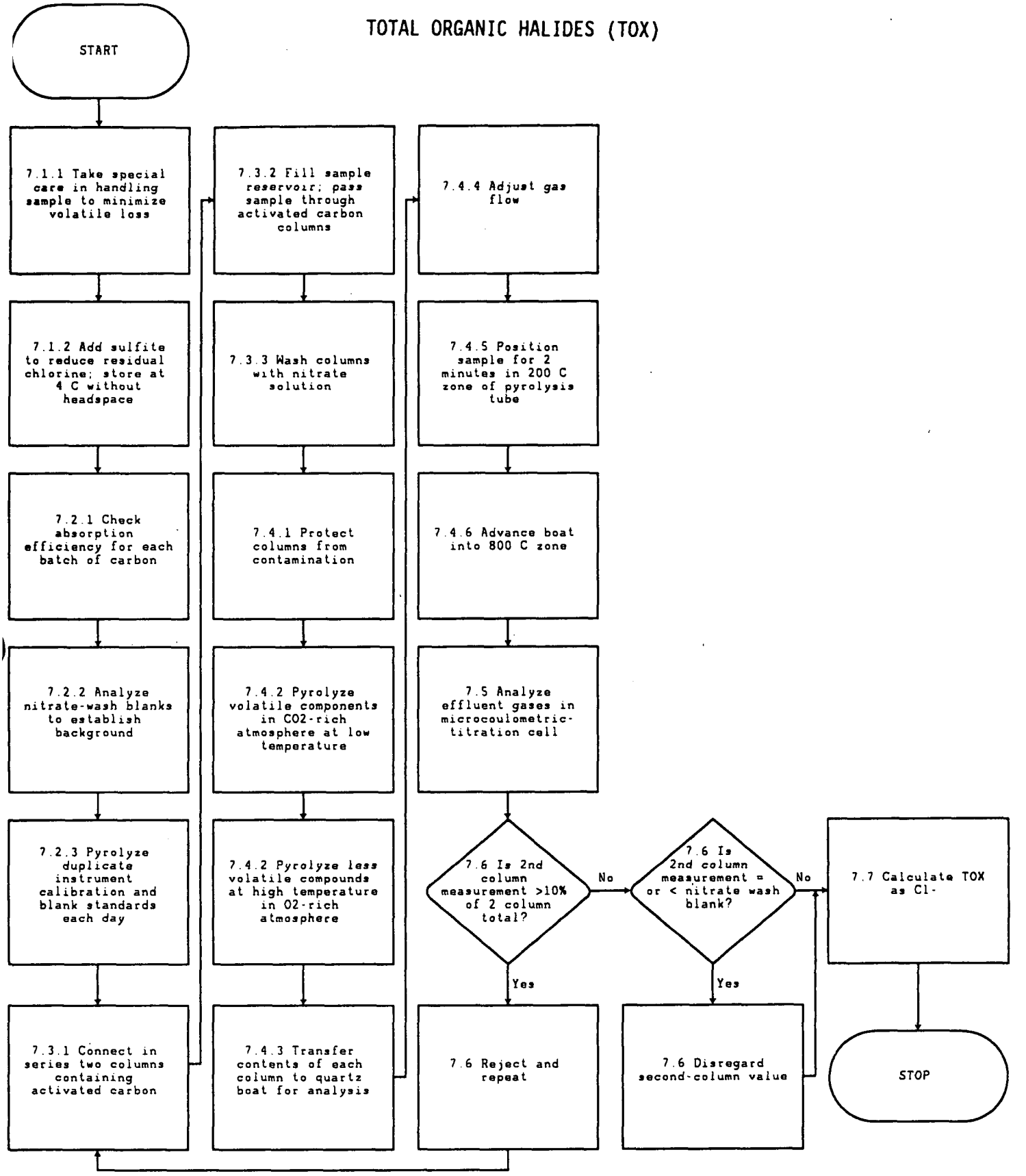


Fig. 2. Flowchart of Analytical System



TOTAL ORGANIC HALIDES (TOX)



METHOD 9021

PURGEABLE ORGANIC HALIDES (POX)

1.0 SCOPE AND APPLICATION

1.1 Method 9021 determines organically bound halides (chloride, bromide, and iodide) purged from a sample of drinking water or ground water. They are reported as chloride. This method is a quick screening procedure requiring about 10 minutes. The method uses a sparging device, a pyrolysis furnace, and a microcoulometric-titration detector.

1.2 Method 9021 detects purgeable organically bound chlorine, bromine, and iodine. Fluorine containing species are not determined by this method. Method 9021 measures POX concentrations ranging from 5 to 1,000 μg/L.

1.3 Method 9021 is restricted to use by, or under the supervision of, analysts experienced in the operation of a pyrolysis/microcoulometer and in the interpretation of the results.

2.0 SUMMARY OF METHOD

2.1 A sample of water, protected against the loss of volatiles by the elimination of headspace in the sampling container, is transferred to a purging vessel. The volatile organic halides are purged into a pyrolysis furnace using a stream of CO_2 and the hydrogen halide (HX) pyrolysis product is trapped and titrated electrolytically using a microcoulometric detector.

3.0 INTERFERENCES

3.1 Contaminants, reagents, glassware, and other sample processing hardware may cause interferences. Method blanks must be routinely run to demonstrate freedom from interferences under the conditions of the analysis.

3.1.1 Glassware must be scrupulously clean. Clean all glassware as soon as possible after use by treating with chromate cleaning solution. This should be followed by detergent washing in hot water. Rinse with tap water and reagent water and dry at 105°C for 1 hour or until dry. Glassware which is not volumetric should, in addition, be heated in a muffle furnace at 300°C for 15 to 30 minutes (Class A volumetric ware should not be heated in a muffle furnace). Glassware should be sealed and stored in a clean environment after drying and cooling to prevent any accumulation of dust or other contaminants.

3.1.2 Use high purity reagents and gases to minimize interference problems.

3.1.3 Avoid using non-PTFE (polytetrafluoroethylene) plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purge gas stream.

3.2 Samples can be contaminated by diffusion of volatile organics (methylene chloride) through the septum seal into the sample during shipment and especially during storage. A trip blank prepared from water and carried through the sampling and handling protocol serves as a check on such contamination. A trip blank should be run with each analytical batch.

3.3 Contamination by carry-over occurs whenever high level and low level samples are sequentially analyzed. To reduce carryover, the purging device and sample syringe must be rinsed with water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high organohalide levels, wash out the purging device with a detergent solution, rinse it with water, and then dry it in a 105°C oven between analyses.

3.4 All operations should be carried out in an area where halogenated solvents, such as methylene chloride, are not being used.

3.5 Residual free chlorine interferes in the method. Free chlorine must be destroyed by adding sodium sulfite when the sample is collected.

4.0 APPARATUS AND MATERIALS

4.1 Sampling equipment (for discrete sampling)

4.1.1 Vial - 25-mL capacity or larger, equipped with a screw-cap with hole in center (Pierce #13075 or equivalent).

4.1.2 Septum - Teflon lined silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and reagent water, and dry at 105°C for 1 hour before use.

4.2 Analytical system

4.2.1 Microcoulometric-titration system containing the following components (a schematic diagram of the microcoulometric-titration system is shown in Figure 1).

4.2.1.1 Purging device.

4.2.1.2 Pyrolysis furnace.

4.2.1.3 Titration cell.

4.2.2 Strip chart recorder (optional) - The recorder is recommended to make sure the peak is down to baselines before stopping integration.

4.2.3 Microsyringes - 10-μL and 25-μL with 0.006 in i.d. needle (Hamilton 702N or equivalent).

4.2.4 Syringe valve - 2 way, with Luer ends.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Sodium sulfide, Na_2S. Granular, anhydrous.

5.4 Acetic acid in water (70%), CH_3COOH. Dilute 7 volumes of glacial acetic acid with 3 volumes of water.

5.5 Sodium chloride calibration standard (1 μg $Cl^-/\mu L$). Dissolve 1.648 g NaCl in water and dilute to 1 liter.

5.6 Carbon dioxide.

5.7 Methanol, CH_3OH. Store away from other solvents.

5.8 Chloroform, $CHCl_3$.

5.9 Chloroform (stock) solution (1 μL = 11.2 μg of $CHCl_3$ or 10 μg Cl^-). Prepare a stock solution by delivering accurately 760 μL (1120 mg) of chloroform into a 100-mL Class A volumetric flask containing approximately 90 mL of methanol. Dilute to volume with methanol (10,000 mg of chlorine/L).

5.10 Chloroform (calibration) solution (1 μL = 0.1 μg Cl^-). Dilute 1 mL of the chloroform stock solution to 100 mL with methanol (100 mg of chlorine/L).

5.11 Chloroform Quality Control (QC) reference sample (100 μg/L). Prepare an aqueous standard by injecting 100 μL of the chloroform calibration standard (100 mg of Cl^-/L) into a Class A volumetric flask containing 100 mL of water. Mix and store in a bottle with zero headspace. Analyze within two hours after preparation.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All samples should be collected in bottles with Teflon lined silicone septa (e.g., Pierce #12722 or equivalent) and be protected from light. If this is not possible, use amber glass 250-mL bottles fitted with Teflon lined caps.

6.3 All glassware must be cleaned prior to use according to the process described in Step 3.1.1.

6.4 Special care should be taken in handling the sample in order to minimize the loss of volatile organohalides. This is accomplished through elimination of headspace and by minimizing the number of transfers.

6.5 Reduce residual chlorine, if present, by adding sodium sulfite (5 mg of sodium sulfite crystals per liter of sample). Sodium sulfite should be added to empty sample bottles at the time of sampling. Shake vigorously for 1 minute after bottle has been filled with sample and properly sealed. Samples should be stored at 4°C without headspace. POX may increase during storage of the sample.

6.6 All samples must be analyzed within 14 days of collection.

7.0 PROCEDURE

7.1 Calibration.

7.1.1 Assemble the sparging/pyrolysis/microcoulometric-titration apparatus shown in Figure 1 in accordance with the manufacturer's specifications. Typically a CO_2 flow of 150 mL/min and a sparger temperature of 45 $\pm$ 5°C are employed. The pyrolysis furnace should be set at 800 $\pm$ 10°C. Attach the titration cell to the pyrolysis tube outlet and fill with electrolyte (70% acetic acid). Flow rate and temperature changes will affect the compounds that are purged and change the percent recovery of marginal compounds. Therefore, these parameters should not be varied. Adjust gas flow rate according to manufacturer's directions.

7.1.2 Turn on the instrument and allow the gas flow and temperatures to stabilize. When the background current of the titration cell has stabilized the instrument is ready for use.

7.1.3 Calibrate the microcoulometric-titration system for Cl^- equivalents by injecting various amounts (1 to 80 μL) of the sodium chloride calibration standard directly into the titration cell and integrating the response using the POX integration mode. If desired, the analog output of the titration cell can be displayed on a strip chart recorder. The range of sodium chloride amounts should cover the range of expected sample concentrations and should always be less than 80 μg of Cl^-. The integrated response should read within 2% or 0.05 μg of the quantity injected (whichever is larger) over the range 1-80 μg Cl^-. If this calibration requirement is not met, then the instrument sensitivity parameters should be adjusted according to the manufacturer's specifications to achieve an accurate response.

7.1.4 Check the performance of the analytical system daily by analyzing three 5-mL aliquots of a freshly prepared 100 μg/L chloroform check standard. The mean of these three analyses should be between 0.4-0.55 μg of Cl^- and the percent relative standard deviation should be 5% or less. If these criteria are not met, the system should be checked as described in the instrument maintenance manual in order to isolate the problem.

NOTE: Low chloroform recovery can often be traced to a vitrified inlet tube. The tube should be checked regularly and the analyst should be able to determine, based on chloroform recoveries, when the tube should be replaced.

7.1.5 Determine an instrument blank daily by running an analysis with the purge vessel empty. The instrument blank should be 0.00 ± 0.05 μg of Cl^-. Analyze a calibration blank sample daily. The calibration blank should be within 0.02 μg of Cl^- of the reagent blank.

7.2 Sample analysis

7.2.1 Select a chloroform spike concentration representative of the expected levels in the samples. Using the chloroform stock solution, prepare a spiking solution in methanol which is 500 times more concentrated than the selected spike concentration. Add 10 μL of the spiking solution to 5-mL aliquots of the samples chosen for spiking (refer to Section 8.0, Quality Control, for guidance in selecting the appropriate number of samples to be spiked).

7.2.2 Allow sample to come to ambient temperature prior to drawing it into the syringe. Remove the plunger from a 5-mL or 10-mL syringe and attach a closed syringe valve. If maximum sensitivity is desired and the sample does not foam excessively, a 10-mL sample aliquot may be analyzed. Otherwise 5-mL aliquots should be used. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5 mL. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data (e.g., accidental spill), or for duplicate analysis.

7.2.3 Attach the syringe valve assembly to the syringe valve on the purging device. Place the pyrolysis/microcoulometer system in the POX integration mode to activate the integration system. Immediately open the syringe valves and inject the sample into the purging chamber.

7.2.4 Close both valves and purge the sample for 10 minutes.

7.2.5 After integration is complete, open the syringe valves and withdraw the purged sample. Flush the syringe and purging device with water prior to analyzing other samples.

7.2.6 If the integrated response exceeds the working range of the instrument, prepare a dilution of the sample from the aliquot in the second syringe with water and reanalyze. The water must meet the criteria of Step 7.1.5. It may be necessary to heat and purge dilution waters.

7.3 Pyrolysis procedure

7.3.1 Pyrolysis of the purged organic component of the sample is accomplished by pyrolyzing in a CO_2-rich atmosphere at a low temperature

to ensure the conversion of brominated trihalomethanes to a titratable species.

7.4 Directly analyze the effluent gases in the microcoulometric-titration cell. Carefully follow instrument manual instructions for optimizing cell performance.

7.5 Calculations - POX as Cl^- is calculated using the following formula:

$$\frac{Q_s}{V} \times 1000 = \mu g/L \text{ Purgeable Organic Halide}$$

where:

Q_s = Quantity of POX as μg of Cl^- in the sample aliquot.
V = Volume of sample aliquot in mL.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection for 3 years. This method is restricted to use by or under supervision of experienced analysts. Refer to the appropriate section of Chapter One for additional quality control guidelines.

8.2 Analyze a minimum of one reagent blank every 20 samples or per analytical batch, whichever is more frequent, to determine if contamination or any memory effects are occurring.

8.3 In addition to the performance check mentioned in Step 7.1.4, verify calibration with an independently prepared chloroform QC reference sample every 15 samples.

8.4 Analyze matrix spiked samples for every 10 samples or analytical batch, whichever is more frequent. The spiked sample is carried through the whole sample preparation process and analytical process.

8.5 Analyze all samples in replicate.

9.0 METHOD PERFORMANCE

9.1 Under conditions of duplicate analysis, the reliable limit of detection is 5 $\mu g/L$.

9.2 Analyses of distilled water, uncontaminated ground water, and ground water from RCRA waste management facilities spiked with volatile chlorinated organics generally give recoveries of 44-128% over the concentration range of 29-4500 $\mu g/L$. Relative standard deviations are generally less than 20% at concentrations greater than 25 $\mu g/L$. These data are shown in Tables 1 and 2.

10.0 REFERENCES

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TABLE 1.
PRECISION AND ACCURACY DATA FOR SELECTED PURGEABLE ORGANIC HALIDES
(Reference 5)

Compound	Dose[1] (μg/L as Cl^-)	Average Recovery (μg/L as Cl^-)	Average Percent Recovery	Standard Deviation	MDL[2] (μg/L)	Number of Replicates
Chloroform	11	11	100	1.4	4.5	7
Trichloroethene	10	6	60	0.7	2.2	7
Tetrachloroethene	10	5	50	0.8	3.2	7
Chlorobenzene	8	3	38	0.6	2.0[3]	7

[1]Ten milliliter aliquot of spiked reagent water analyzed.

[2]The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.

[3]Practical MDL probably greater (approximately 5 to 6 μg/L) due to low recovery.

TABLE 2.
PRECISION AND ACCURACY DATA FOR VARIOUS WATER SAMPLES
(Reference 5)

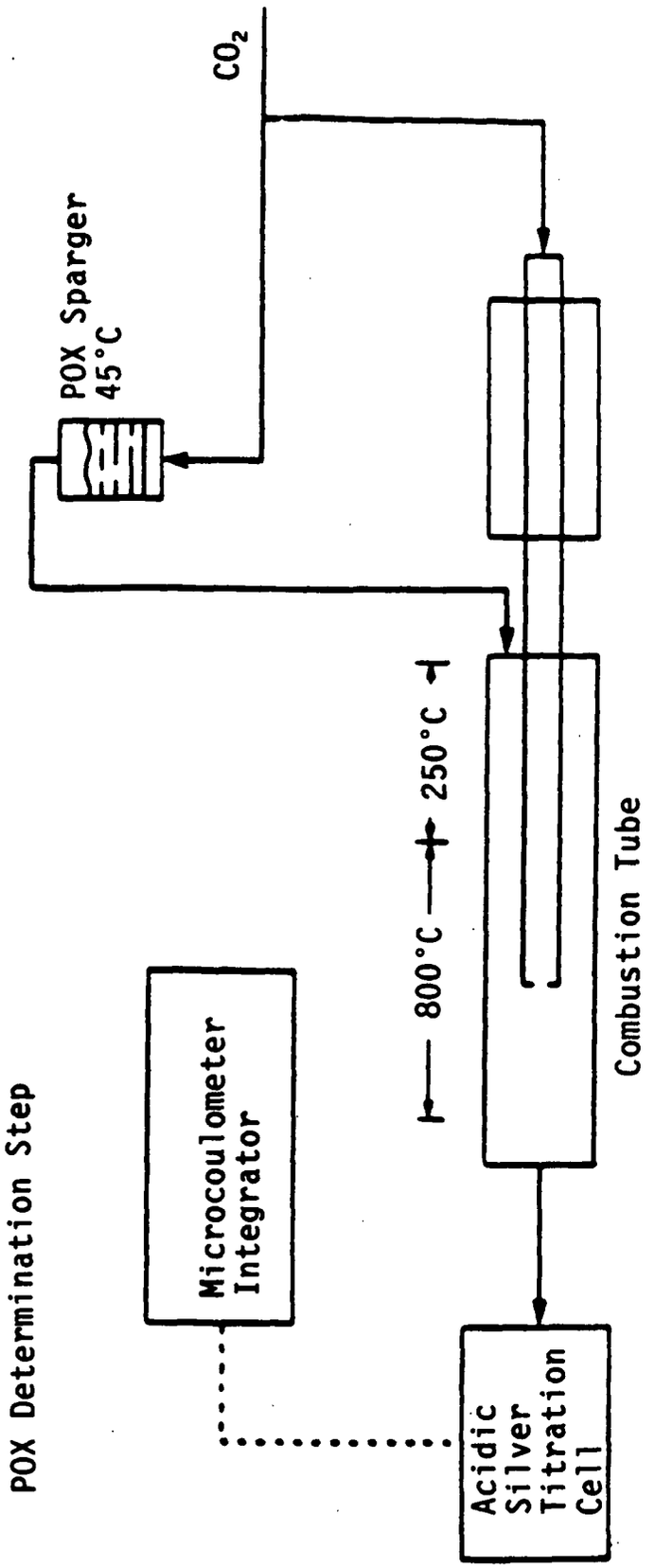
Sample[1]	Background Spike Component	Level ($\mu g/L$ as Cl^-)	Spike Level ($\mu g/L$ as Cl^-)	Average Percent Recovery	Standard Deviation	Number of Replicates
Tap Water	---	---	0	---	2	3
POTW Sewage	Chloroform	68	29	128	5	3
Chlorinated Hydrocarbon Plant Wastewater	Chloroform	114	460	77	36	3
Chlorinated Hydrocarbon Plant Wastewater	Chloroform	32	1,500	50	32	3
Chlorinated Hydrocarbon Plant Wastewater	Chloroform	32	4,500	87	470	3
Solid Waste[2] Leachate	1,1-Dichloro-ethane	171	800	41	17	3
Industrial Wastewater	Methylene chloride	510	800	65	120	3
Aniline[3] Wastewater	Chloroform	15,700	15,000	150	58	3
Aniline[3] Wastewater	Chloroform	15,700	45,000	91	400	3

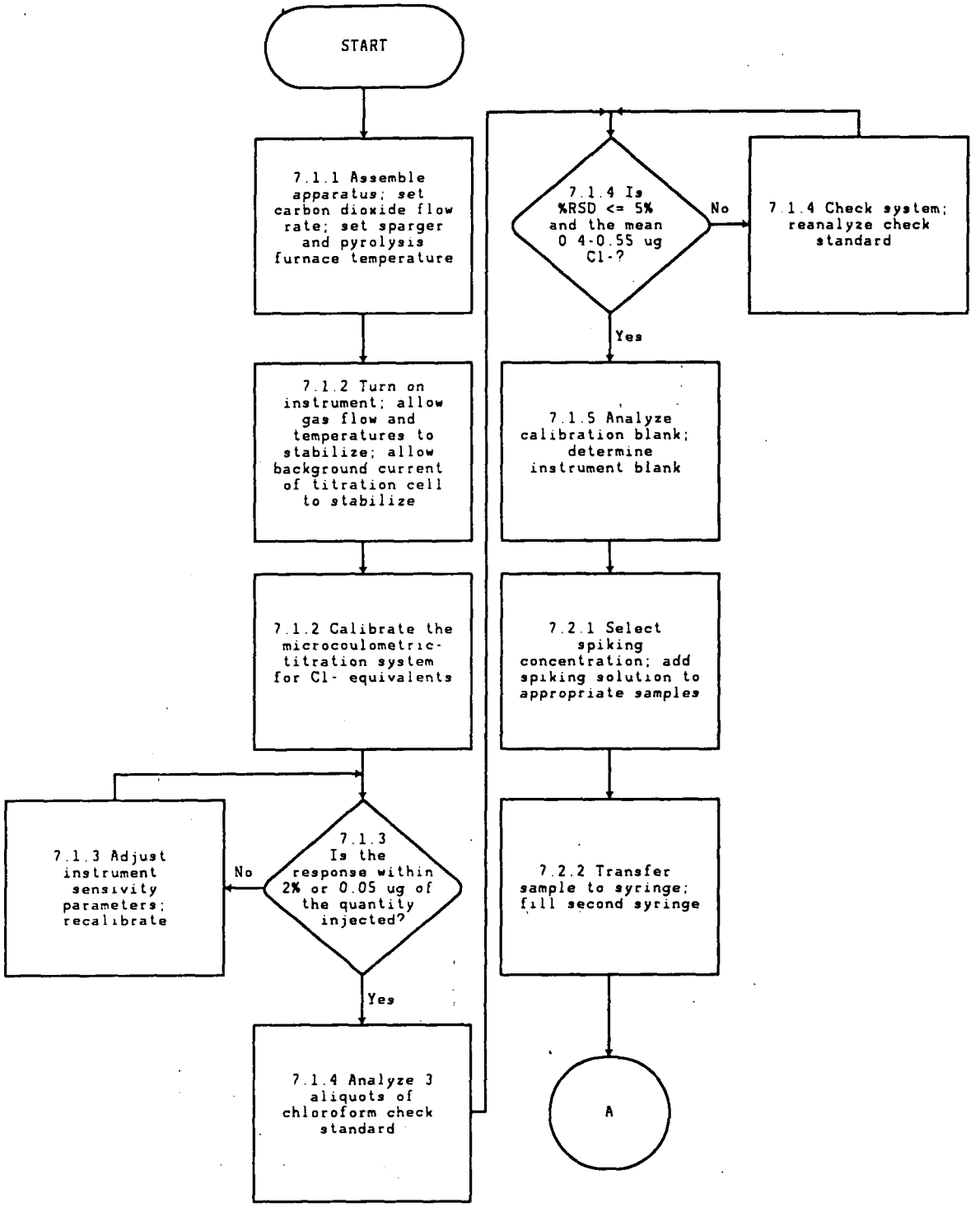
[1]Five milliliter sample aliquots analyzed.

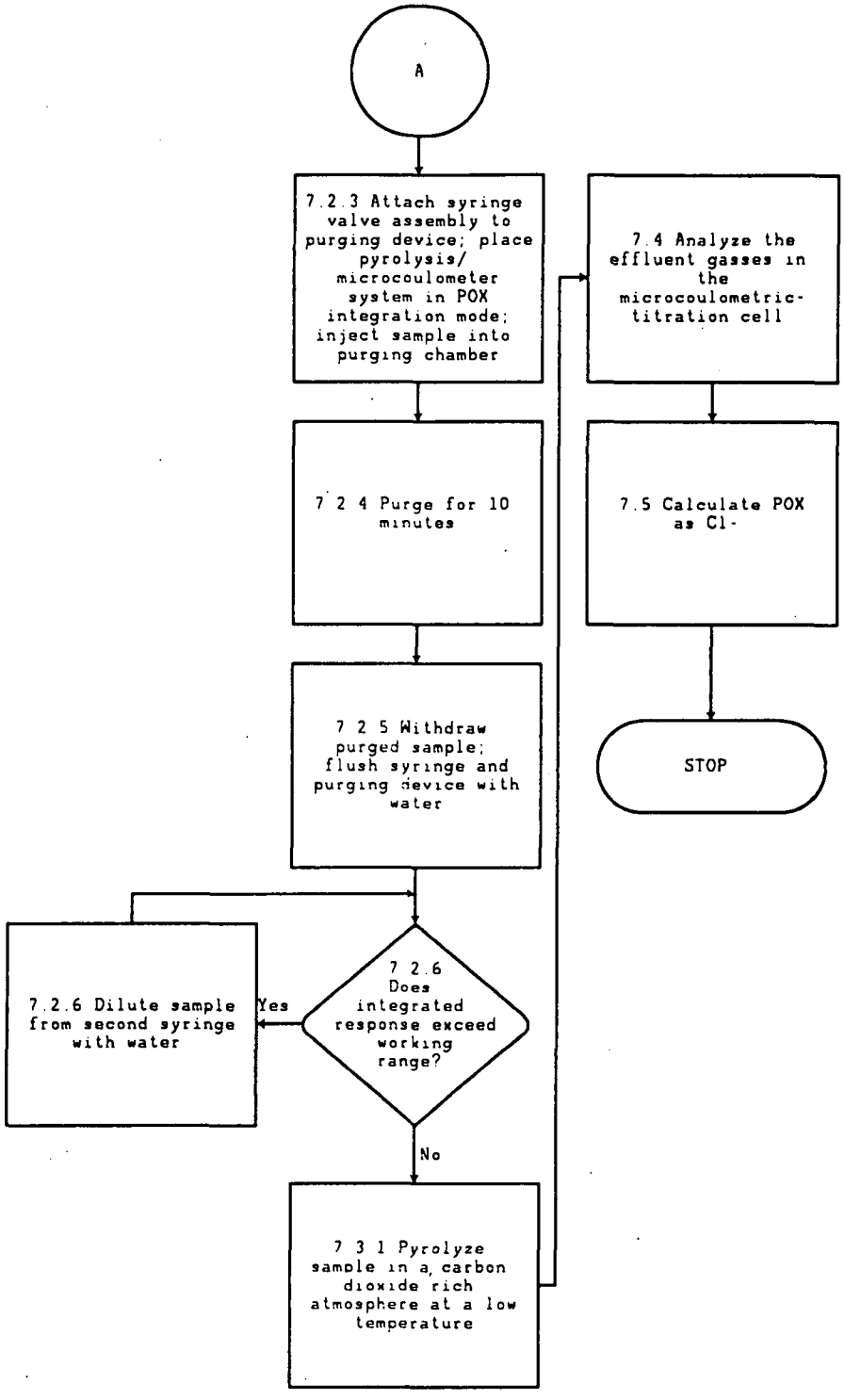
[2]Diluted 200:1 prior to analysis. Values for this sample are in mg/L for original sample.

[3]Diluted 10:1 prior to analysis. Values are for undiluted sample.

FIGURE 1.
MICROCOULOMETRIC - TITRATION SYSTEM




START
7.1.1 Assemble apparatus; set carbon dioxide flow rate; set sparger and pyrolysis furnace temperature
7.1.2 Turn on instrument; allow gas flow and temperatures to stabilize; allow background current of titration cell to stabilize
7.1.2 Calibrate the microcoulometric-titration system for Cl- equivalents
7.1.3 Is the response within 2% or 0.05 ug of the quantity injected?
No
7.1.3 Adjust instrument sensivity parameters; recalibrate
Yes
7.1.4 Analyze 3 aliquots of chloroform check standard
7.1.4 Is %RSD <= 5% and the mean 0.4-0.55 ug Cl-?
No
7.1.4 Check system; reanalyze check standard
Yes
7.1.5 Analyze calibration blank; determine instrument blank
7.2.1 Select spiking concentration; add spiking solution to appropriate samples
7.2.2 Transfer sample to syringe; fill second syringe
A


A
7.2.3 Attach syringe valve assembly to purging device; place pyrolysis/ microcoulometer system in POX integration mode; inject sample into purging chamber
7.4 Analyze the effluent gasses in the microcoulometric-titration cell
7 2 4 Purge for 10 minutes
7.5 Calculate POX as Cl-
7 2 5 Withdraw purged sample; flush syringe and purging device with water
STOP
7.2.6 Dilute sample from second syringe with water
Yes
7 2 6 Does integrated response exceed working range?
No
7 3 1 Pyrolyze sample in a carbon dioxide rich atmosphere at a low temperature

METHOD 9022

TOTAL ORGANIC HALIDES (TOX) BY NEUTRON ACTIVATION ANALYSIS

1.0 SCOPE AND APPLICATION

1.1 Method 9022 determines Total Organic Halides (TOX) in aqueous samples. The method uses a carbon adsorption procedure identical to that of Method 9020 (TOX analysis using a microcoulometric-titration detector), irradiation by neutron bombardment, and then detection using a gamma-ray detector.

1.2 Method 9022 detects all organic halides containing chlorine, bromine, and iodine that are adsorbed by granular activated carbon under the conditions of the method. Each halogen can be quantitated independently.

1.3 Method 9022 is restricted to use by, or under the supervision of, analysts experienced in the operation of neutron activation analysis and familiar with spectral interferences.

1.4 This method, which may be used in place of Method 9020, has the advantage of determining the individual concentrations of the halogens chlorine, bromine, and iodine in addition to TOX.

2.0 SUMMARY OF METHOD

2.1 A sample of water that has been protected against the loss of volatiles by the elimination of headspace in the sampling container, and that is free of undissolved solids, is passed through a column containing 40 mg of granular activated carbon (GAC). The column is washed to remove any trapped inorganic halides. The GAC sample is exposed to thermal neutron bombardment, creating a radioactive isotope. Gamma-ray emission, which is unique to each halogen, is counted. The areas of the resulting peaks are directly proportional to the concentrations of the halogens.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by treating with chromatic cleaning solution. This should be followed by detergent washing in hot water. Rinse with tap water and distilled water and drain dry; glassware which is not volumetric should, in addition, be heated in a muffle furnace at

400°C for 15 to 30 min. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed and stored in a clean environment after drying and cooling to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high-purity reagents and gases helps to minimize interference problems.

3.2 Purity of the activated carbon must be verified before use. Only carbon samples that register less than 2,000 ng Cl^-/40 mg GAC should be used. The stock of activated carbon should be stored in its granular form in a glass container with a Teflon seal. Exposure to the air must be minimized, especially during and after milling and sieving the activated carbon. No more than a 2-wk supply should be prepared in advance. Protect carbon at all times from all sources of halogenated organic vapors. Store prepared carbon and packed columns in glass containers with Teflon seals.

4.0 APPARATUS AND MATERIALS

4.1 Adsorption system (a general schematic of the adsorption system is shown in Figure 1):

4.1.1 **Adsorption module** with pressurized sample and nitrate-wash reservoirs.

4.1.2 **Adsorption columns:** Pyrex, 5-cm long x 6-mm O.D. x 2-mm I.D.

4.1.3 **Granular activated carbon** (GAC): Filtrasorb-400, Calgon-APC or equivalent, ground or milled, and screened to a 100/200 mesh range. Upon combustion of 40 mg of GAC, the apparent halide background should be 1000 ng Cl^- equivalent or less.

4.1.4 **Cerafelt** (available from Johns-Manville) or equivalent: Form this material into plugs using a 2-mm-I.D. stainless steel borer with ejection rod to hold 40 mg of GAC in the adsorption columns.

CAUTION: Do not touch this material with your fingers. Oily residue will contaminate carbon.

4.1.5 **Column holders.**

4.1.6 **Volumetric flasks:** 100-mL, 50-mL.

4.2 Containers suitable for containment of samples and standards during irradiation (e.g., 1/5-dram polyethylene snap-cap vial).

4.3 Sample introduction system and a reactor generating a thermal neutron flux capable of achieving enough halogen activity for counting purposes (e.g., a reactor having a neutron flux of 5 x 10^{12} neutrons/cm^2/sec).

4.4 A gamma-ray detector and data-handling system capable of resolving the halogen peaks from potential interferences and background.

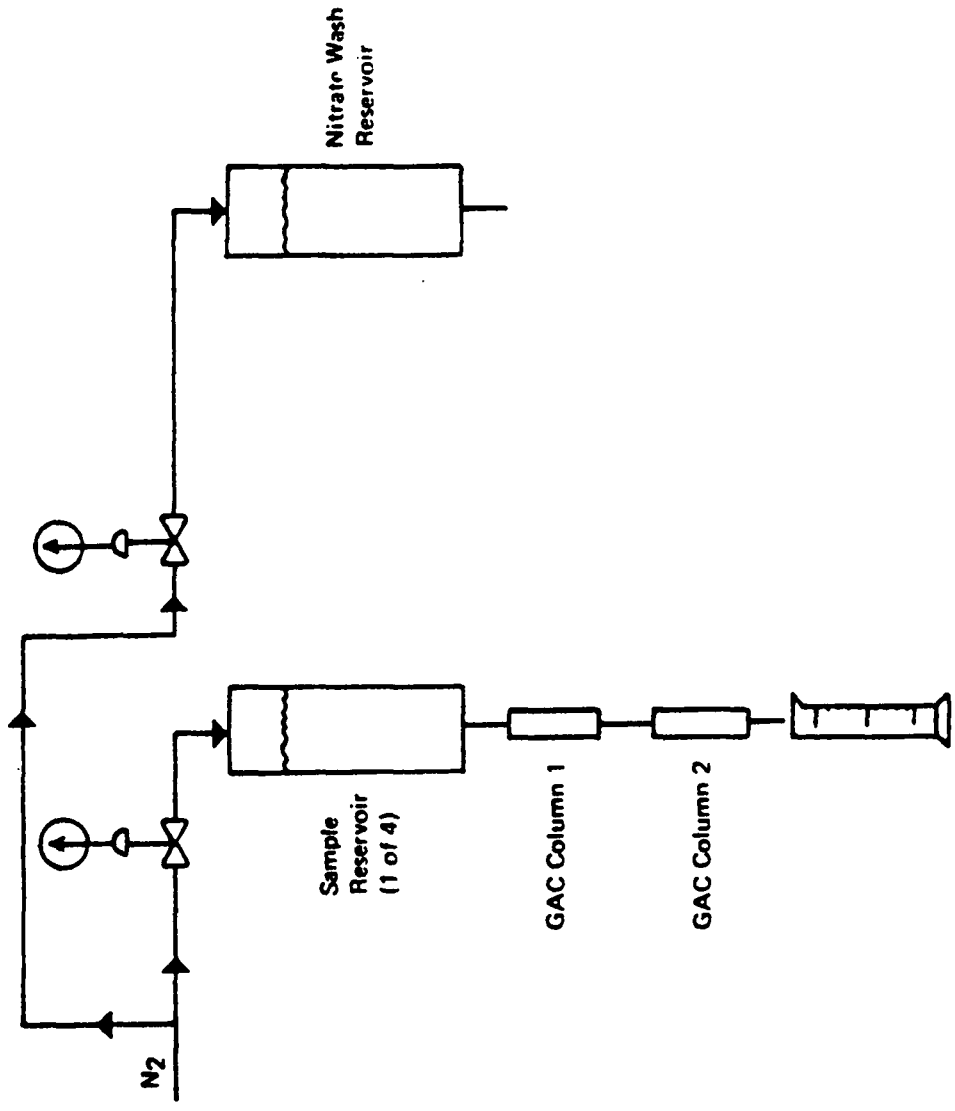


Figure 1. Schematic diagram of adsorption system.

5.0 REAGENTS

5.1 Prepurified nitrogen.

5.2 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.3 Nitrate-wash solution (5,000 mg NO_3^-/L): Prepare a nitrate-wash solution by transferring approximately 8.2 g of potassium nitrate (KNO_3) into a 1-liter volumetric flask and diluting to volume with Type II water.

5.4 Acetone and nanograde hexane (50% v/v mixture).

5.5 Sodium sulfite, 0.1 M (ACS reagent grade, 12.6 g/L).

5.6 Concentrated nitric acid (HNO_3): Reagent grade.

5.7 Standards: 25-ug Cl, 2.5-ug Br, and 2.5-ug I.

5.8 Radioactive standards to be used for calibrating gamma-ray detection systems.

5.9 Trichlorophenol solution, stock (1 uL = 10 ug Cl^-): Prepare a stock solution by accurately weighing accurately 1.856 g of trichlorophenol into a 100-mL volumetric flask. Dilute to volume with methanol.

5.10 Trichlorophenol standard, adsorption efficiency (100 ug Cl^-/liter): Prepare an adsorption-efficiency standard by injecting 10 uL of stock solution into 1 liter of Type II water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All samples should be collected in bottles with Teflon septa (e.g., Pierce #12722 or equivalent) and be protected from light. If this is not possible, use amber glass, 250-mL, fitted with Teflon-lined caps. Foil may be substituted for Teflon if the sample is not corrosive. Samples must be protected against loss of volatiles by eliminating headspace in the container. Containers must be washed and muffled at 400°C before use, to minimize contamination.

6.3 All glassware must be dried prior to use according to the method discussed in Paragraph 3.1.1.

7.0 PROCEDURE

7.1 Sample preparation:

7.1.1 Special care should be taken in handling the sample in order to minimize the loss of volatile organohalides. The adsorption procedure should be performed simultaneously on the front and back columns.

7.1.2 Reduce residual chlorine by adding sulfite (1 mL of 0.1 M sulfite per liter of sample). Sulfite should be added at the time of sampling if the analysis is meant to determine the TOX concentration at the time of sampling. It should be recognized that TOX may increase on storage of the sample. Samples should be stored at 4°C without headspace.

7.1.3 Samples containing undissolved solids should be centrifuged and decanted.

7.1.4 Adjust the pH of the sample to approximately 2 with concentrated HNO_3 just prior to adding the sample to the reservoir.

7.2 Calibration:

7.2.1 Check the adsorption efficiency of each newly prepared batch of carbon by analyzing 100 mL of the adsorption efficiency standard, in duplicate, along with duplicates of the blank standard. The net recovery should be within 5% of the standard value.

7.2.2 Nitrate-wash blanks (method blanks): Establish the repeatability of the method background each day by first analyzing several nitrate-wash blanks. Monitor this background by spacing nitrate-wash blanks between each group of eight analysis determinations. The nitrate-wash blank values are obtained on single columns packed with 40 mg of activated carbon. Wash with the nitrate solution, as instructed for sample analysis, and then analyze the carbon.

7.2.3 Prior to each day's operation, calibrate the instrument using radioactive standards (e.g., cobalt-60 and radium-226 sources). The instrument is calibrated such that gamma rays from the standards fall within one channel of their true energies. A 100-sec blank is then counted to verify that no stray radioactive sources are within sensing distance of the detector. As data are obtained throughout the day, peak locations in the standards are monitored to ensure there is no electronic drift of the instrument. If drift is noted, the system must be recalibrated.

7.3 Adsorption procedure:

7.3.1 Connect in series two columns, each containing 40 mg of 100/200-mesh activated carbon.

7.3.2 Fill the sample reservoir and pass a metered amount of sample through the activated-carbon columns at a rate of approximately 3 mL/min.

NOTE: 100 mL of sample is the preferred volume for concentrations of TOX between 5 and 500 ug/L, 50 mL for 501 to 1000 ug/L, and 25 mL for 1,001 to 2,000 ug/L.

7.3.3 Wash the columns-in-series with at least 2 mL of the 5,000-mg/L nitrate solution at a rate of approximately 2 mL/min to displace inorganic chloride ions.

7.4 Activation:

7.4.1 After the quartz collection tube with the GAC is removed from the extraction unit, the GAC and cerafelt pads are extruded, using the packing rod, into a prewashed plastic container (e.g., 1/5-dram polyethylene snap-cap vial). The vial has been prewashed to remove inorganic and organic chlorine by a soak in distilled water, followed by storage in a glass jar containing 50% v/v acetone and hexane. After extrusion, the vial is removed by forceps and air-dried to remove residual water, acetone, and hexane. After extrusion, the vial is snapped shut, the hinge removed with a scalpel blade, the cap heat-sealed to the vial with an electric soldering gun reserved for that purpose, and a single-digit number placed on the vial with a marker pen.

7.4.2 Samples plus a similar vial containing 25 ug Cl, 2.5 ug Br, and 2.5 ug I standards are then introduced into the reactor, generally by placing them together in a 5-dram polyethylene vial and inserting them into a pneumatic-tube transfer "rabbit" for neutron irradiation. Irradiation is typically for a 15-min period at a thermal neutron irradiation flux of 5×10^{12} neutrons/cm^2/sec. After returning from the reactor, the rabbit is allowed to "cool" for 20 min to allow short-lived radioisotopes (primarily Al) present in the GAC to decay.

7.5 Detection:

7.5.1 Analysis is performed using a lithium-drifted germanium [Ge(Li)] gamma-ray detector with an amplifier and a 4096-channel memory unit for data storage. The analyses can be performed either manually, with the operator changing samples and transferring the data to magnetic tape, or automatically, with both functions performed by an automatic sample changer.

7.5.2 Analysis begins by counting the standard and samples for a suitable time period (e.g., 200-sec "live" time for the standards and samples). The operator records the time intervals between samples and the "dead" time of each sample in a logbook for later use in calculating halogen concentrations in each sample.

7.5.3 Breakthrough: The unpredictable nature of the background bias makes it especially difficult to recognize the extent of breakthrough of organohalides from one column to another. All second-

column measurements for a properly operating system should not exceed 10% of the two-column total measurement. If the 10% figure is exceeded, one of three events could have happened: (1) the first column was overloaded and a legitimate measure of breakthrough was obtained, in which case taking a smaller sample may be necessary; (2) channeling or some other failure occurred, in which case the sample may need to be rerun; or (3) a high random bias occurred, and the result should be rejected and the sample rerun. Because it may not be possible to determine which event occurred, a sample analysis should be repeated often enough to gain confidence in results. As a general rule, any analysis that is rejected should be repeated whenever a sample is available. In the event that repeated analyses show that the second column consistently exceeds the 10% figure and the total is too low for the first column to be saturated and the inorganic Cl is less than 20,000 times the organic chlorine value, then the result should be reported, but the data user should be informed of the problem. If the second-column measurement is equal to or less than the nitrate-wash blank value, the second-column value should be disregarded.

7.6 Calculations:

7.6.1 Chlorine, bromine, and iodine can be analyzed within a 200-sec counting period taking place 20 to 40 min after irradiation.

7.6.2 Chlorine is analyzed using the 1642-KeV gamma ray produced by 37.1-min ^{38}Cl. Bromine is analyzed using the 616-KeV gamma ray from 17.7-min ^{80}Br, and iodine is analyzed using the 442-KeV gamma ray produced by 25-min ^{128}I.

7.6.3 The calculation used for quantitation is:

$$\text{ppm halogen} = \frac{\text{cts unk.}}{\text{cts std.}} \times \frac{\text{counting time std.}}{\text{counting time unk.}} \times \frac{\text{ug in std.}}{\text{sample vol.}} \times e^{\lambda t}$$

where:

cts unk. = the integrated area of the appropriate gamma-ray peak in the unknown with background subtracted and the total multiplied by 1 + [(% dead time unknown - % dead time std.)/200]. The latter correction is usually less than 4% and corrects for pile-up errors.

cts std. = the integrated area of the appropriate gamma-ray peak in the standard with background subtracted.

counting time std. = the "live" counting time in seconds of the standard.

counting time unk. = the "live" counting time in seconds of the unknown.

ug in std. = the number of micrograms of the stable element in question in the standard (25 for Cl, 2.5 for Br and I).

sample vol. = the volume of sample passed through the GAC column, in mL.

$e^{\lambda t}$ = the decay correction to bring all statistics back to $t = 0$; $\lambda = 0.693/t_{1/2}$, where $t_{1/2}$ = the half-life in minutes.

t = the time interval in minutes from the end of the count of the standard until the end of the count of the sample.

7.6.4 No further calculations are necessary as long as the final sample is counted within 40 min after the end of irradiation.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this procedure by analyzing appropriate quality-control check samples.

8.3 The laboratory must develop and maintain a statement of method accuracy for their laboratory. The laboratory should update the accuracy statement regularly as new recovery measurements are made.

8.4 Employ a minimum of one blank per sample batch to determine if contamination is occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

8.7 It is recommended that the laboratory adopt additional quality-assurance practices for use with this method. The specific practices that would be most productive will depend upon the needs of the laboratory and the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance-evaluation studies.

8.8 Quality control for the analysis phase is very straightforward in as much as the instrument is a noncontact analyzer. That is, only the radiation emitted from the sample -- not the sample itself -- should touch the analyzer.

Because contamination of the system is not usually a problem (unless a sample spills on it), the most serious quality-control issues deal with uniform neutron flux, counting geometry, and spectral interpretation. The amount of radioactivity induced in a sample is directly proportional to the neutron flux it is exposed to. Because this flux can vary depending on how the sample is positioned in relation to the reactor core during irradiation, it is essential that a known standard be irradiated with every sample batch to act as a flux monitor. Care must also be taken to ensure that the standard and all samples associated with the standard are counted at the same distance from the detector.

9.0 METHOD PERFORMANCE

9.1 The following statistics are based on seven replicate analyses:

		Chlorine	Bromine	Iodine	Combined average	Pooled
River water	$\bar{x}$	38.2	17	<1	55.2	0.18
		0.16	0.076	---	---	0.18
Well water	$\bar{x}$ (ppb)	50.7	4.7	<1	55.4	---
		0.30	0.038	---	55.2	0.30
WWTP effluent	$\bar{x}$	242	35.2	20.4	539.6	---
		0.56	0.033	0.23	---	0.61

9.2 The reliable limits of detection are 5 ppb for chlorine and 1 ppb for iodine and bromine.

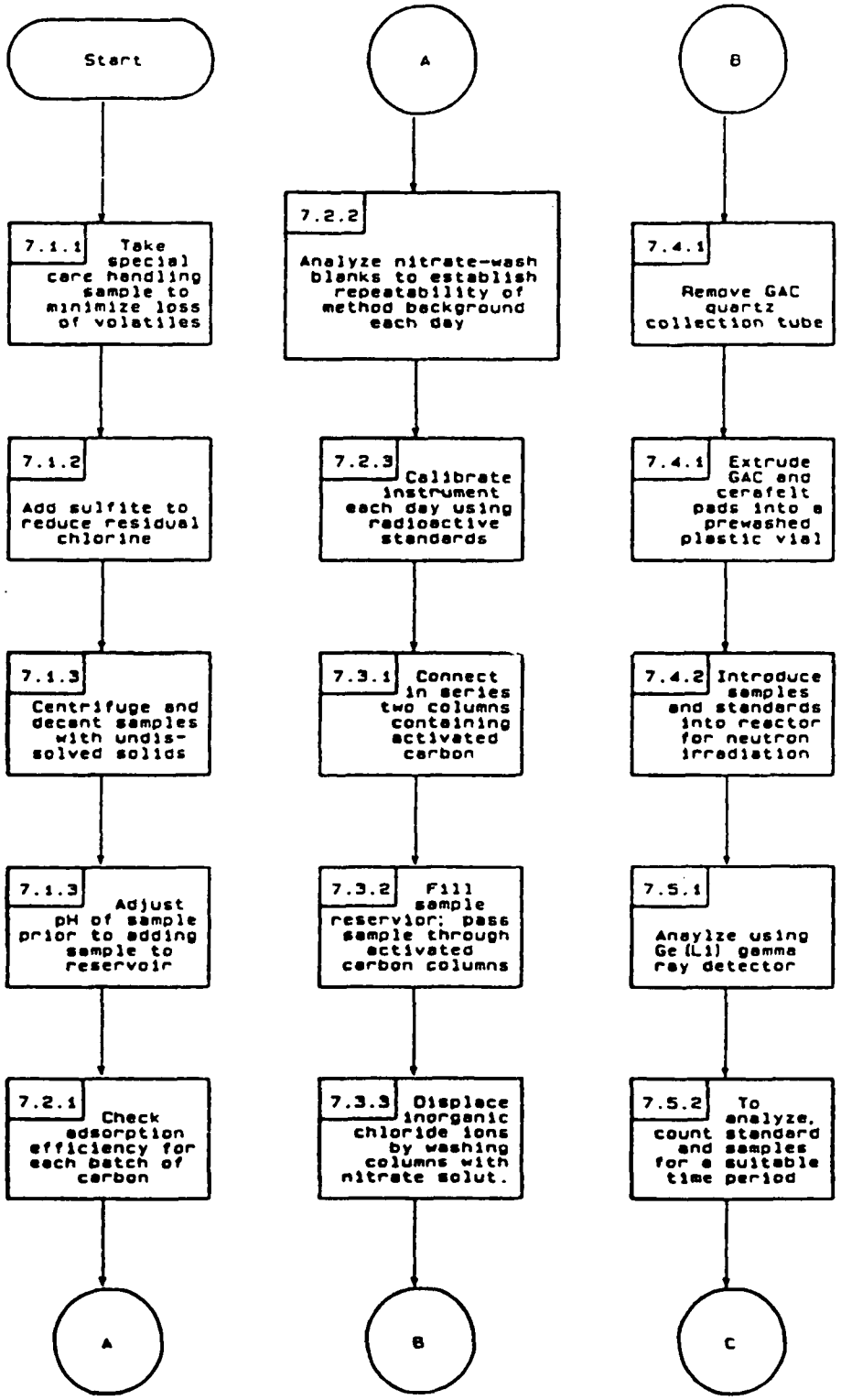
10.0 REFERENCES

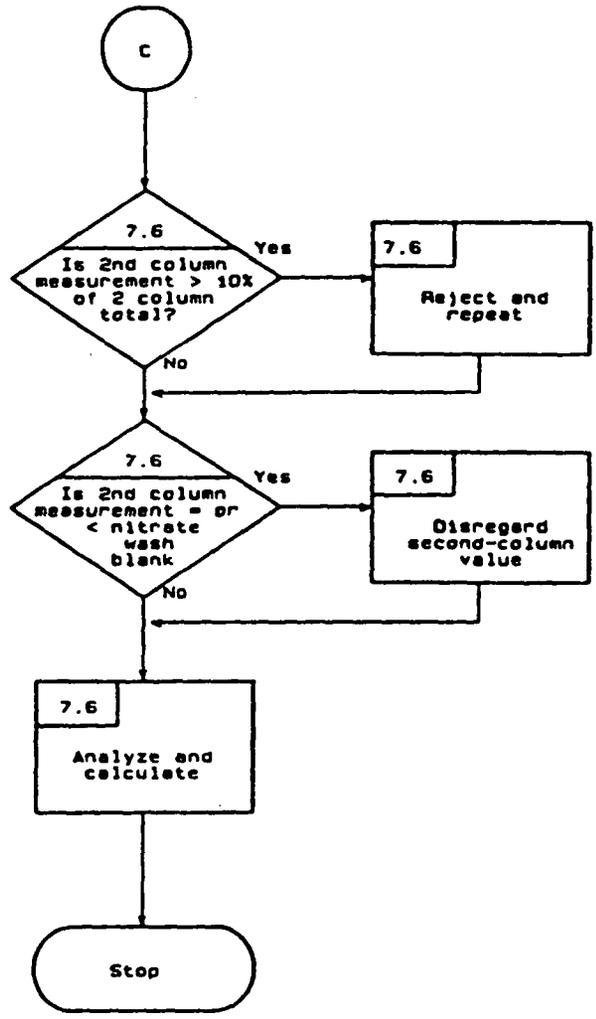
None required.

METHOD 9022

TOTAL ORGANIC HALIDES (TOX) BY

NEUTRON ACTIVATION ANALYSIS




C
7.6
Is 2nd column measurement > 10% of 2 column total?
Yes
7.6
Reject and repeat
No
7.6
Is 2nd column measurement = or < nitrate wash blank
Yes
7.6
Disregard second-column value
No
7.6
Analyze and calculate
Stop

METHOD 9030A

ACID-SOLUBLE AND ACID-INSOLUBLE SULFIDES

1.0 SCOPE AND APPLICATION

1.1 The distillation procedure described in this method is designed for the determination of sulfides in aqueous, solid waste materials, or effluents.

1.2 This method provides only a semi-quantitative determination of sulfide compounds considered "acid-insoluble" (e.g., CuS and SnS_2) in solid samples. Recovery has been shown to be 20 to 40% for CuS, one of the most stable and insoluble compounds, and 40 to 60% for SnS_2 which is slightly more soluble.

1.3 This method is not applicable to oil or multiphasic samples or samples not amenable to the distillation procedure which can be analyzed by Method 9031.

1.4 Method 9030 is suitable for measuring sulfide concentrations in samples which contain between 0.2 and 50 mg/kg of sulfide.

1.5 This method is not applicable for distilling reactive sulfide, however, Method 9030 is used to quantify the concentration of sulfide from the reactivity test. Refer to Chapter Seven, Step 7.3.4.1 for the determination of reactive sulfide.

1.6 This method measures total sulfide which is usually defined as the acid-soluble fraction of a waste. If, however, one has previous knowledge of the waste and is concerned about both soluble sulfides such as H_2S, and metal sulfides, such as CuS and SnS_2, then total sulfide is defined as the combination of both acid-soluble and acid-insoluble fractions. For wastes where only metal sulfides are suspected to be present, only the acid-insoluble fraction needs to be performed.

2.0 SUMMARY OF METHOD

2.1 For acid-soluble sulfide samples, separation of sulfide from the sample matrix is accomplished by the addition of sulfuric acid to the sample. The sample is heated to 70°C and the hydrogen sulfide (H_2S) which is formed is distilled under acidic conditions and carried by a nitrogen stream into zinc acetate gas scrubbing bottles where it is precipitated as zinc sulfide.

2.2 For acid-insoluble sulfide samples, separation of sulfide from the sample matrix is accomplished by suspending the sample in concentrated hydrochloric acid by vigorous agitation. Tin(II) chloride is present to prevent oxidation of sulfide to sulfur by the metal ion (as in copper(II)), by the matrix, or by dissolved oxygen in the reagents. The prepared sample is distilled under acidic conditions at 100°C under a stream of nitrogen. Hydrogen sulfide gas is released from the sample and collected in gas scrubbing bottles containing zinc(II) and a strong acetate buffer. Zinc sulfide precipitates.

2.3 The sulfide in the zinc sulfide precipitate is oxidized to sulfur with a known excess amount of iodine. Then the excess iodine is determined by titration with a standard solution of phenyl arsine oxide (PAO) or sodium thiosulfate until the blue iodine starch complex disappears. As the use of standard sulfide solutions is not possible because of oxidative degradation, quantitation is based on the PAO or sodium thiosulfate.

3.0 INTERFERENCES

3.1 Aqueous samples must be taken with a minimum of aeration to avoid volatilization of sulfide or reaction with oxygen, which oxidizes sulfide to sulfur compounds that are not detected.

3.2 Reduced sulfur compounds, such as sulfite and hydrosulfite, decompose in acid, and may form sulfur dioxide. This gas may be carried over to the zinc acetate gas scrubbing bottles and subsequently react with the iodine solution yielding false high values. The addition of formaldehyde into the zinc acetate gas scrubbing bottles removes this interference. Any sulfur dioxide entering the scrubber will form an addition compound with the formaldehyde which is unreactive towards the iodine in the acidified mixture. This method shows no sensitivity to sulfite or hydrosulfite at concentrations up to 10 mg/kg of the interferant.

3.3 Interferences for acid-insoluble sulfides have not been fully investigated. However, sodium sulfite and sodium thiosulfate are known to interfere in the procedure for soluble sulfides. Sulfur also interferes because it may be reduced to sulfide by tin(II) chloride in this procedure.

3.4 The iodometric method suffers interference from reducing substances that react with iodine, including thiosulfate, sulfite, and various organic compounds.

3.5 The insoluble method should not be used for the determination of soluble sulfides because it can reduce sulfur to sulfide, thus creating a positive interference.

4.0 APPARATUS AND MATERIALS

4.1 Gas evolution apparatus as shown in Figure 1

4.1.1 Three neck flask - 500-mL, 24/40 standard taper joints.

4.1.2 Dropping funnel - 100-mL, 24/40 outlet joint.

4.1.3 Purge gas inlet tube - 24/40 joint, with coarse frit.

4.1.4 Purge gas outlet - 24/40 joint reduced to 1/4 in. tube.

4.1.5 Gas scrubbing bottles - 125-mL, with 1/4 in. o.d. inlet and outlet tubes. Impinger tube must be fritted.

4.1.6 Tubing - 1/4 in. o.d. Teflon or polypropylene. Do not use rubber.

NOTE: When analyzing for acid-insoluble sulfides, the distillation apparatus is identical to that used in the distillation procedure for acid-soluble sulfides except that the tubing and unions downstream of the distillation flask must be all Teflon, polypropylene or other material resistant to gaseous HCl. The ground glass joints should be fitted with Teflon sleeves to prevent seizing and to prevent gas leaks. Pinch clamps should also be used on the joints to prevent leaks.

4.2 Hot plate stirrer.

4.3 pH meter.

4.4 Nitrogen regulator.

4.5 Flowmeter.

4.6 Top-loading balance - capable of weighing 0.1 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Zinc acetate solution for sample preservation (2N), $Zn(CH_3COO)_2 \cdot 2H_2O$. Dissolve 220 g of zinc acetate dihydrate in 500 mL of reagent water.

5.4 Sodium hydroxide (1N), NaOH. Dissolve 40 g of NaOH in reagent water and dilute to 1 liter.

5.5 Formaldehyde (37% solution), CH_2O. This solution is commercially available.

5.6 Zinc acetate for the scrubber

5.6.1 For acid-soluble sulfides: Zinc acetate solution (approximately 0.5M). Dissolve about 110 g zinc acetate dihydrate in 200 mL of reagent water. Add 1 mL hydrochloric acid (concentrated), HCl, to prevent precipitation of zinc hydroxide. Dilute to 1 liter.

5.6.2 For acid-insoluble sulfides: Zinc acetate/sodium acetate buffer. Dissolve 100 g sodium acetate, $NaC_2H_3O_2$, and 11 g zinc acetate dihydrate in 800 mL of reagent water. Add 1 mL concentrated hydrochloric acid and dilute to 1 liter. The resulting pH should be 6.8.

5.7 Acid to acidify the sample

5.7.1 For acid-soluble sulfides: Sulfuric acid (concentrated), H_2SO_4.

5.7.2 For acid-insoluble sulfides: Hydrochloric acid (9.8N), HCl. Place 200 mL of reagent water in a 1-liter beaker. Slowly add concentrated HCl to bring the total volume to 1 liter.

5.8 Starch solution - Use either an aqueous solution or soluble starch powder mixtures. Prepare an aqueous solution as follows. Dissolve 2 g soluble starch and 2 g salicylic acid, $C_7H_6O_3$, as a preservative, in 100 mL hot reagent water.

5.9 Nitrogen.

5.10 Iodine solution (approximately 0.025N)

5.10.1 Dissolve 25 g potassium iodide, KI, in 700 mL of reagent water in a 1-liter volumetric flask. Add 3.2 g iodine, I_2. Allow to dissolve. Add the type and amount of acid specified in Step 7.3.2. Dilute to 1 liter and standardize as follows.

5.10.2 Dissolve approximately 2 g KI in 150 mL of reagent water. Add exactly 20 mL of the iodine solution (Step 5.10.1) to be titrated and dilute to 300 mL with reagent water.

5.10.3 Titrate with 0.025N standardized phenylarsine oxide or 0.025N sodium thiosulfate until the amber color fades to yellow. Add starch indicator solution. Continue titration drop by drop until the blue color disappears.

5.10.4 Run in replicate.

5.10.5 Calculate the normality as follows.

$$\text{Normality } (I_2) = \frac{\text{mL of titrant x normality of titrant}}{\text{sample size in mL}}$$

5.11 Sodium sulfide nonanhydrate, $Na_2S \cdot 9H_2O$. For the preparation of standard solutions to be used for calibration curves. Standards must be prepared at pH > 9 and < 11. Protect standard from exposure to oxygen by preparing it without headspace. These standards are unstable and should be prepared daily.

5.12 Tin(II) chloride, $SnCl_2$, granular.

5.13 Titrant.

5.13.1 Standard phenylarsine oxide solution (PAO) (0.025N), C_6H_5AsO. This solution is commercially available.

CAUTION: PAO is toxic.

5.13.2 Standard sodium thiosulfate solution (0.025N), $Na_2S_2O_3 \cdot 5H_2O$. Dissolve 6.205 $\pm$ 0.005 g $Na_2S_2O_3 \cdot 5H_2O$ in 500 mL reagent water. Add 9 mL 1N NaOH and dilute to 1 liter.

5.14 Sodium hydroxide (6N), NaOH. Dissolve 240 g of sodium hydroxide in 1 liter of reagent water.

5.15 Hydrochloric acid (6N), HCl. Place 51 mL of reagent water in a 100 mL Class A volumetric flask. Slowly add concentrated HCl to bring the total volume to 100 mL.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All aqueous samples and effluents must be preserved with zinc acetate and sodium hydroxide. Use four drops of 2N zinc acetate solution per 100 mL of sample. Adjust the pH to greater than 9 with 6N sodium hydroxide solution. Fill the sample bottle completely and stopper with a minimum of aeration. The treated sample is relatively stable and can be held for up to seven days. If high concentrations of sulfide are expected to be in the sample, continue adding zinc acetate until all the sulfide has precipitated. For solid samples, fill the surface of the solid with 2N zinc acetate until moistened. Samples must be cooled to 4°C and stored headspace free.

6.3 Sample Preparation

6.3.1 For an efficient distillation, the mixture in the distillation flask must be of such a consistency that the motion of the stirring bar is sufficient to keep the solids from settling. The mixture must be free of solid objects that could disrupt the stirring bar. Prepare the sample using one of the procedures in this section then proceed with the distillation step (Section 7.0).

6.3.2 If the sample is aqueous, shake the sample container to suspend any solids, then quickly decant the appropriate volume (up to 250 mL) of the sample to a graduated cylinder, weigh the cylinder, transfer to the distillation flask and reweigh the cylinder to the nearest milligram. Be sure that a representative aliquot is used, or use the entire sample.

6.3.3 If the sample is aqueous but contains soft clumps of solid, it may be possible to break the clumps and homogenize the sample by placing the sample container on a jar mill and tumble or roll the sample for a few hours. The slurry may then be aliquotted and weighed as above to the nearest milligram then diluted with reagent water up to a total volume of 250 mL to produce a mixture that is completely suspended by the stirring bar.

6.3.4 If the sample is primarily aqueous, but contains a large proportion of solid, the sample may be roughly separated by phase and the amount of each phase measured and weighed to the nearest milligram into

the distillation flask in proportion to their abundance in the sample. Reagent water may be added up to a total volume of 250 mL. As a guideline, no more than 25 g dry weight or 50 g of sludge can be adequately suspended in the apparatus.

6.3.5 If the sample contains solids which absorb water and swell, limit the sample size to 25 g dry weight. Otherwise, the solids will restrict the fluid motion and lower the recovery.

6.3.6 If the sample contains solid objects that cannot be reduced in size by tumbling, the solids must be broken manually. Clay-like solids should be cut with a spatula or scalpel in a crystallizing dish. If the solids can be reduced to a size that they can be suspended by the stirring bar, the solid and liquid can be proportionately weighed.

6.3.7 Non-porous harder objects, for example stones or pieces of metal, may be weighed and discarded. The percent weight of non-porous objects should be reported and should be used in the calculation of sulfide concentration if it has a significant effect on the reported result.

7.0 PROCEDURE

For acid-soluble sulfide samples, go to 7.1
For acid-insoluble sulfide samples, go to 7.2

7.1 Acid-Soluble Sulfide

7.1.1 In a preliminary experiment, determine the approximate amount of sulfuric acid required to adjust a measured amount of the sample to pH less than or equal to 1. The sample size should be chosen so that it contains between 0.2 and 50 mg of sulfide. Place a known amount of sample or sample slurry in a beaker. Add reagent water until the total volume is 200 mL. Stir the mixture and determine the pH. Slowly add sulfuric acid until the pH is less than or equal to 1. Discard this preliminary sample.

CAUTION: Toxic hydrogen sulfide may be generated from the acidified sample. This operation must be performed in the hood and the sample left in the hood until the sample has been made alkaline or the sulfide has been destroyed. From the amount of sulfuric acid required to acidify the sample and the mass or volume of the sample acidified, calculate the amount of acid required to acidify the sample to be placed in the distillation flask.

7.1.2 Prepare the gas evolution apparatus as shown in Figure 1 in a fume hood.

7.1.2.1 Prepare a hot water bath at 70°C by filling a crystallizing dish or other suitable container with water and place it on a hot plate stirrer. Place a thermometer in the bath and monitor the temperature to maintain the bath at 70°C.

7.1.2.2 Assemble the three neck 500-mL flask, fritted gas inlet tube, and exhaust tube. Use Teflon sleeves to seal the ground glass joints. Place a Teflon coated stirring bar into the flask.

7.1.2.3 Place into each gas scrubbing bottle 10 ± 0.5 mL of the 0.5M zinc acetate solution, 5.0 ± 0.1 mL of 37% formaldehyde and 100 ± 5.0 mL reagent water.

7.1.2.4 Connect the gas evolution flask and gas scrubbing bottles as shown in Figure 1. Secure all fittings and joints.

7.1.3 Carefully place an accurately weighed sample which contains 0.2 to 50 mg of sulfide into the flask. If necessary, dilute to approximately 200 mL with reagent water.

7.1.4 Place the dropping funnel onto the flask making sure its stopcock is closed. Add the volume of sulfuric acid calculated in Step 7.1.1 plus an additional 50 mL into the dropping funnel. The bottom stopcock must be closed.

7.1.5 Attach the nitrogen inlet to the top of the dropping funnel gas shut-off valve. Turn on the nitrogen purge gas and adjust the flow through the sample flask to 25 mL/min. The nitrogen in the gas scrubbing bottles should bubble at about five bubbles per second. Nitrogen pressure should be limited to approximately 10 psi to prevent excess stress on the glass system and fittings. Verify that there are no leaks in the system. Open the nitrogen shut-off valve leading to the dropping funnel. Observe that the gas flow into the sample vessel will stop for a short period while the pressure throughout the system equalizes. If the gas flow through the sample flask does not return within a minute, check for leaks around the dropping funnel. Once flow has stabilized, turn on magnetic stirrer. Purge system for 15 minutes with nitrogen to remove oxygen.

7.1.6 Heat sample to 70°C. Open dropping funnel to a position that will allow a flow of sulfuric acid of approximately 5 mL/min. Monitor the system until most of the sulfuric acid within the dropping funnel has entered the sample flask. Solids which absorb water and swell will restrict fluid motion and, therefore, lower recovery will be obtained. Such samples should be limited to 25 g dry weight.

7.1.7 Purge, stir, and maintain a temperature of 70°C for a total of 90 minutes from start to finish. Shut off nitrogen supply. Turn off heat.

7.1.8 Proceed to Step 7.3 for the analysis of the zinc sulfide by titration.

7.2 Acid-Insoluble Sulfide

7.2.1 As the concentration of HCl during distillation must be within a narrow range for successful distillation of H_2S, the water content must be controlled. It is imperative that the final concentration of HCl in the distillation flask be about 6.5N and that the sample is mostly suspended in the fluid by the action of the stirring bar. This is achieved by adding 50 mL of reagent water, including water in the sample, 100 mL of 9.8N HCl, and the sample to the distillation flask. Solids which absorb water and swell will restrict fluid motion and, therefore, lower recovery will be obtained. Such samples should be limited to 25 g dry weight. Other samples can range from 25 to 50 g.

7.2.2 If the matrix is a dry solid, weigh a portion of the sample such that it contains 0.2 to 50 mg of sulfide. The solid should be crushed to reduce particle size to 1 mm or less. Add 50 mL of reagent water.

7.2.3 If the matrix is aqueous, then a maximum of 50 g of the sample may be used. No additional water may be added. As none of the target compounds are volatile, drying the sample may be preferable to enhance the sensitivity by concentrating the sample. If less than 50 g of the sample is required to achieve the 0.2 to 50 mg of sulfide range for the test, then add reagent water to a total volume of 50 mL.

7.2.4 If the matrix is a moist solid, the water content of the sample must be determined (Karl Fischer titration, loss on drying, or other suitable means) and the water in the sample included in the total 50 mL of water needed for the correct HCl concentration. For example, if a 20 g sample weight is needed to achieve the desired sulfide level of 0.2 to 50 mg and the sample is 50% water then 40 mL rather than 50 mL of reagent water is added along with the sample and 100 mL of 9.8N HCl to the distillation flask.

7.2.5 Weigh the sample and 5 g $SnCl_2$ into the distillation flask. Use up to 50 mL of reagent water, as calculated above, to rinse any glassware.

7.2.6 Assemble the distillation apparatus as in Figure 1. Place 100 $\pm$ 2.0 mL of zinc acetate/sodium acetate buffer solution and 5.0 $\pm$ 0.1 mL of 37% formaldehyde in each gas scrubbing bottle. Tighten the pinch clamps on the distillation flask joints.

7.2.7 Make sure the stopcock is closed and then add 100 $\pm$ 1.0 mL of 9.8N HCl to the dropping funnel. Connect the nitrogen line to the top of the funnel and turn the nitrogen on to pressurize the dropping funnel headspace.

7.2.8 Set the nitrogen flow at 25 mL/min. The nitrogen in the gas scrubbing bottles should bubble at about five bubbles per second. Purge the oxygen from the system for about 15 minutes.

7.2.9 Turn on the magnetic stirrer. Set the stirring bar to spin as fast as possible. The fluid should form a vortex. If not, the distillation will exhibit poor recovery. Add all of the HCL from the dropping funnel to the flask.

7.2.10 Heat the water bath to the boiling point (100°C). The sample may or may not be boiling. Allow the purged distillation to proceed for 90 minutes at 100°C. Shut off nitrogen supply. Turn off heat.

7.2.11 Proceed to Step 7.3 for the analysis of the zinc sulfide by titration.

7.3 Titration of Distillate

7.3.1 Pipet a known amount of standardized 0.025N iodine solution (See Step 5.10.5) in a 500-mL flask, adding an amount in excess of that needed to oxidize the sulfide. Add enough reagent water to bring the volume to 100 mL. The volume of standardized iodine solution should be about 65 mL for samples with 50 mg of sulfide.

7.3.2 If the distillation for acid-soluble sulfide is being used, add 2 mL of 6N HCl. If the distillation for acid-insoluble sulfides is performed, 10 mL of 6N HCl should be added to the iodine.

7.3.3 Pipet both of the gas scrubbing bottle solutions to the flask, keeping the end of the pipet below the surface of the iodine solution. If at any point in transferring the zinc acetate solution or rinsing the bottles, the amber color of the iodine disappears or fades to yellow, more 0.025N iodine must be added. This additional amount must be added to the amount from Step 7.3.1 for calculations. Record the total volume of standardized 0.025N iodine solution used.

7.3.4 Prepare a rinse solution of a known amount of standardized 0.025N iodine solution, 1 mL of 6N HCl, and reagent water to rinse the remaining white precipitate (zinc sulfide) from the gas scrubbing bottles into the flask. There should be no visible traces of precipitate after rinsing.

7.3.5 Rinse any remaining traces of iodine from the gas scrubbing bottles with reagent water, and transfer the rinsate to the flask.

7.3.6 Titrate the solution in the flask with standard 0.025N phenylarsine oxide or 0.025N sodium thiosulfate solution until the amber color fades to yellow. Add enough starch indicator for the solution to turn dark blue and titrate until the blue disappears. Record the volume of titrant used.

7.3.7 Calculate the concentration of sulfide using the following equation:

$$\frac{(\text{mL } I_2 \times \text{N } I_2) - (\text{mL titrant} \times \text{N titrant}) \times \left(\frac{32.06 \text{ g}}{2 \text{ eq.}}\right)}{\text{sample weight (kg) or sample volume (L)}} = \text{sulfide (mg/kg) or (mg/L)}$$

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by or under supervision of experienced analysts. Refer to the appropriate section of Chapter One for additional quality control guidelines.

8.2 A reagent blank should be run once in twenty analyses or per analytical batch, whichever is more frequent.

8.3 Check standards are prepared from water and a known amount of sodium sulfide. A check standard should be run with each analytical batch of samples, or once in twenty samples. Acceptable recovery will depend on the level and matrix.

8.4 A matrix spiked sample should be run for each analytical batch or twenty samples, whichever is more frequent, to determine matrix effects. If recovery is low, acid-insoluble sulfides are indicated. A matrix spiked sample is a sample brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

9.1 Accuracy - Accuracy for this method was determined by three independent laboratories by measuring percent recoveries of spikes for both clean matrices (water) and actual waste samples. The results are summarized below.

<u>For Acid-Soluble Sulfide</u>

Accuracy of titration step only
  Lab A 84-100% recovery
  Lab B 110-122% recovery
Accuracy for entire method for clean matrices (H_2O)
  Lab C 94-106% recovery
Accuracy of entire method for actual waste samples
  Lab C 77-92% recovery

Spiking levels ranged from 0.4 to 8 mg/L

<u>For Acid-Insoluble Sulfide</u>

The percent recovery was not as thoroughly studied for acid-insoluble sulfide as it was for acid-soluble sulfide.

Accuracy of entire method for synthetic waste samples
Lab C 21-81% recovery

Spiking levels ranged from 2.2 to 22 mg/kg

9.2 Precision

For Acid-Soluble Sulfide

Precision of titration step only
Lab A CV% 2.0 to 37
Lab B CV% 1.1 to 3.8
Precision of entire method for clean matrices (H_2O)
Lab C CV% 3.0 to 12
Precision of entire method for actual waste samples
Lab C CV% 0.86 to 45

For Acid-Insoluble Sulfide

Precision of entire method with synthetic wastes
Lab C CV 1.2 to 42

9.3 Detection Limit - The detection limit was determined by analyzing seven replicates at 0.45 and 4.5 mg/L. The detection limit was calculated as the standard deviation times the student's t-value for a one-tailed test with n-1 degrees of freedom at 99% confidence level. The detection limit for a clean matrix (H_2O) was found to be between 0.2 and 0.4 mg/L.

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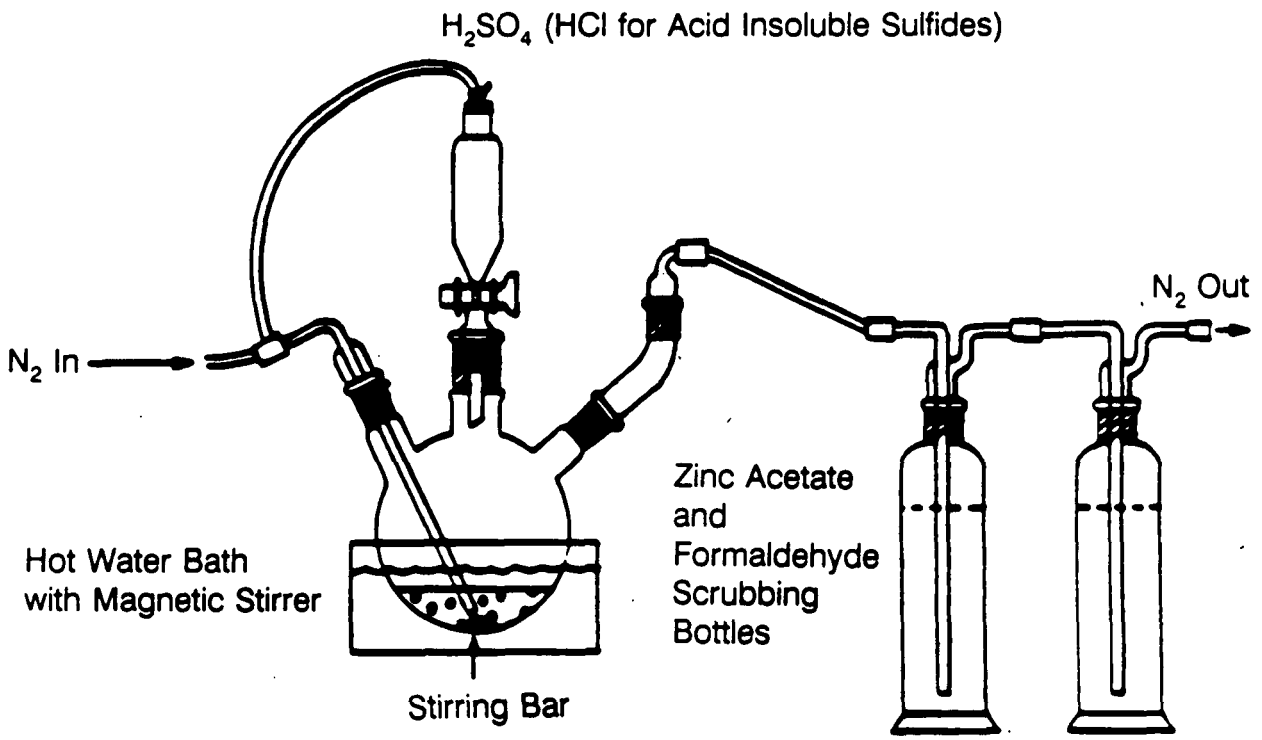
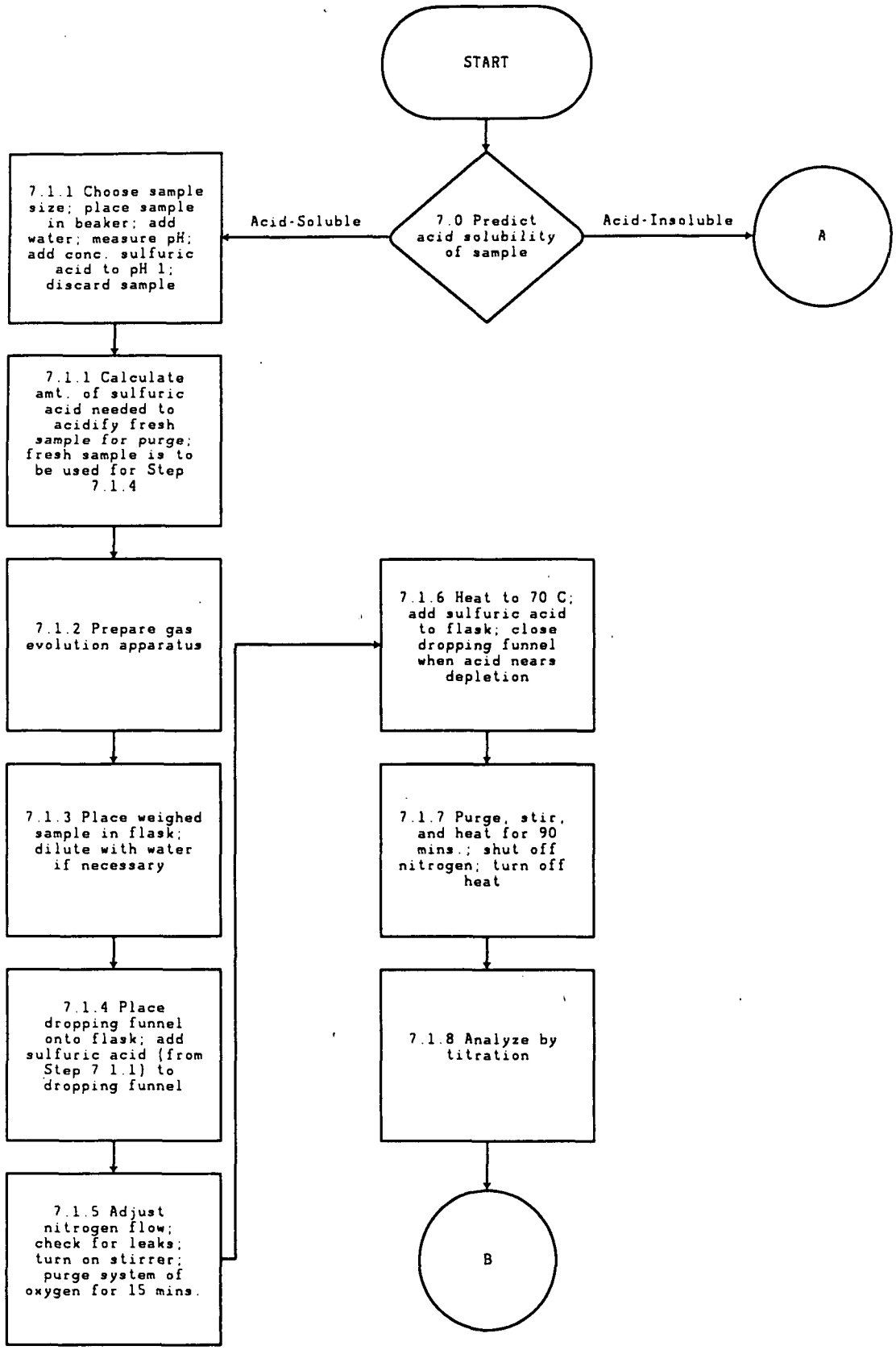
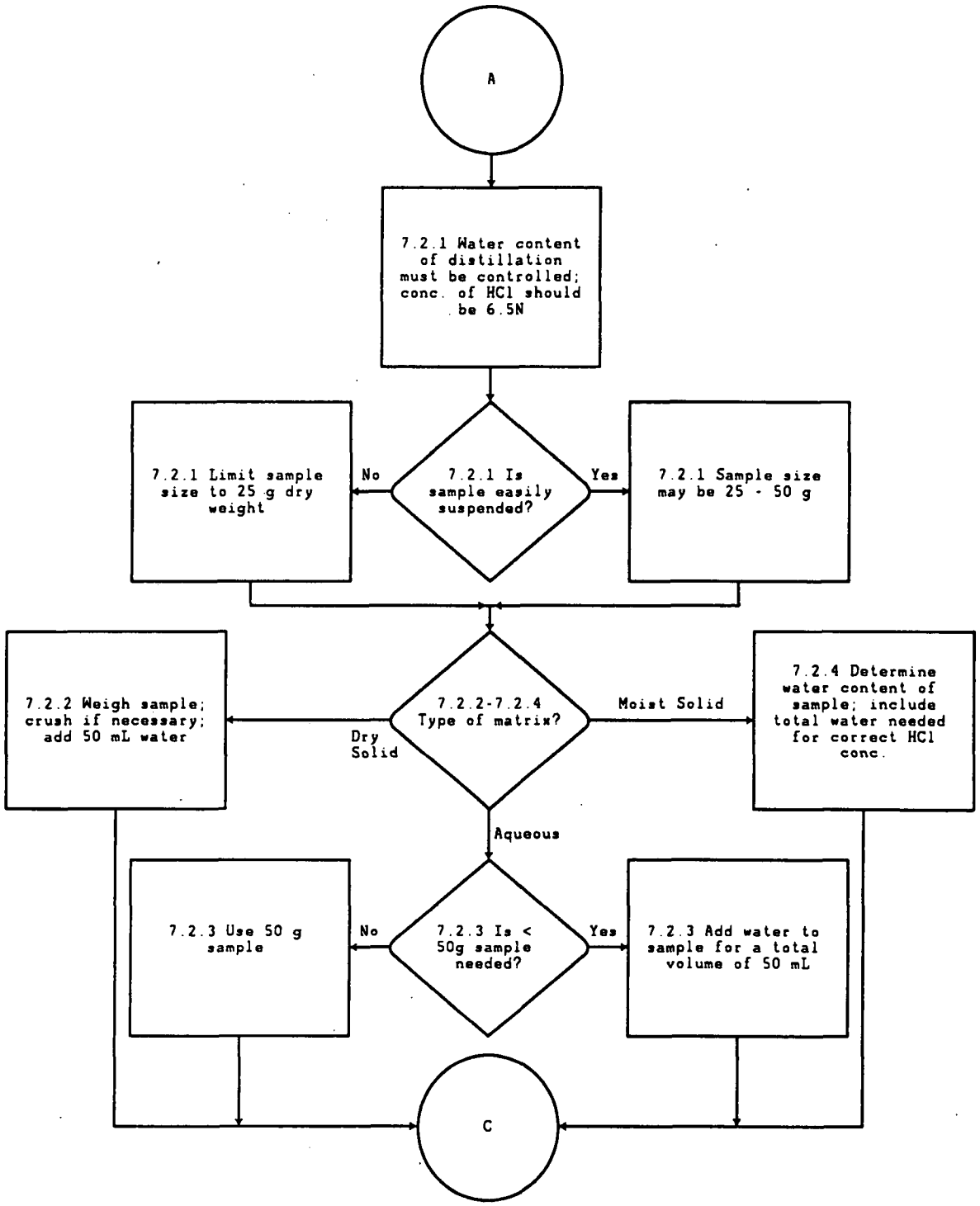
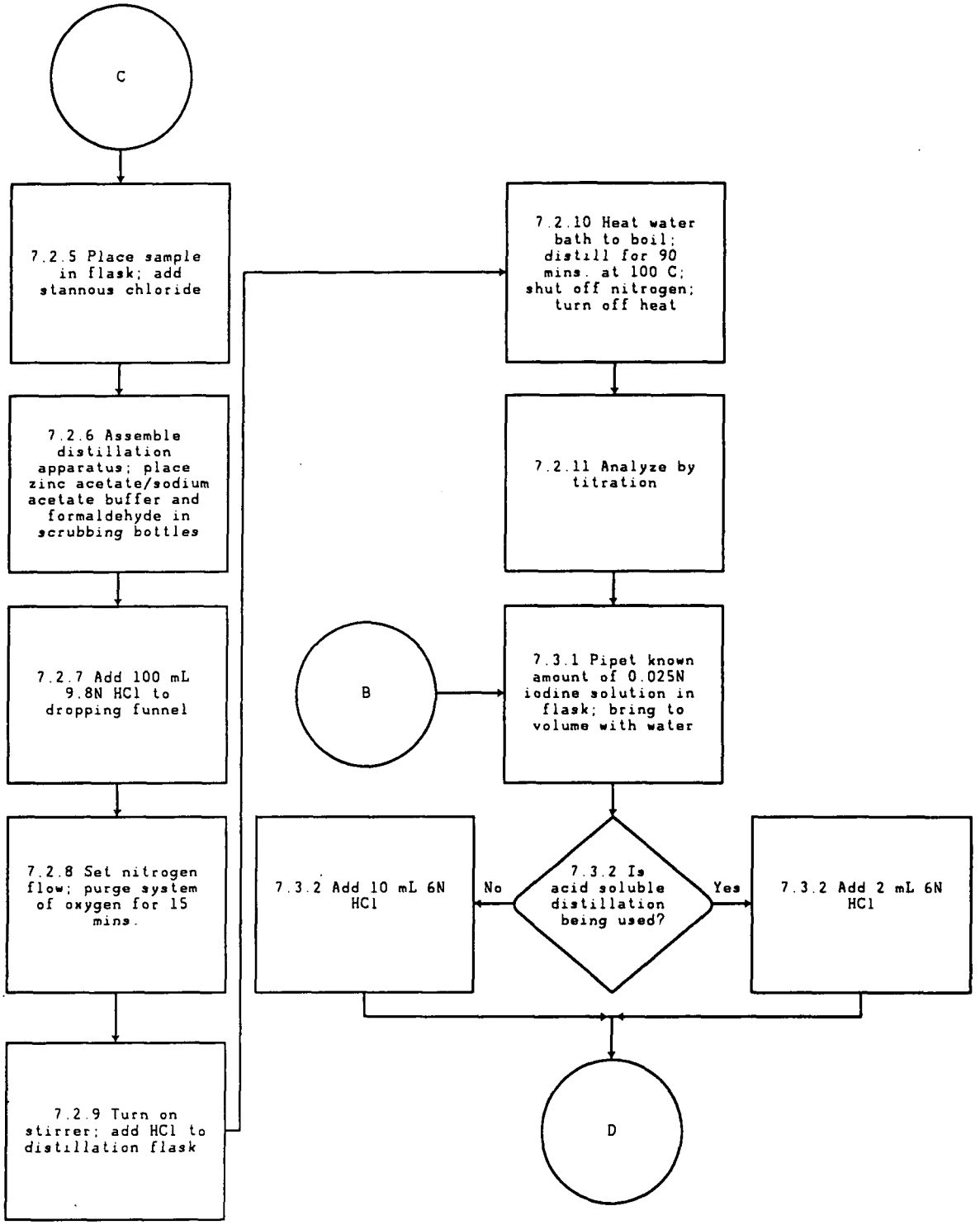
FIGURE 1.
GAS EVOLUTION APPARATUS

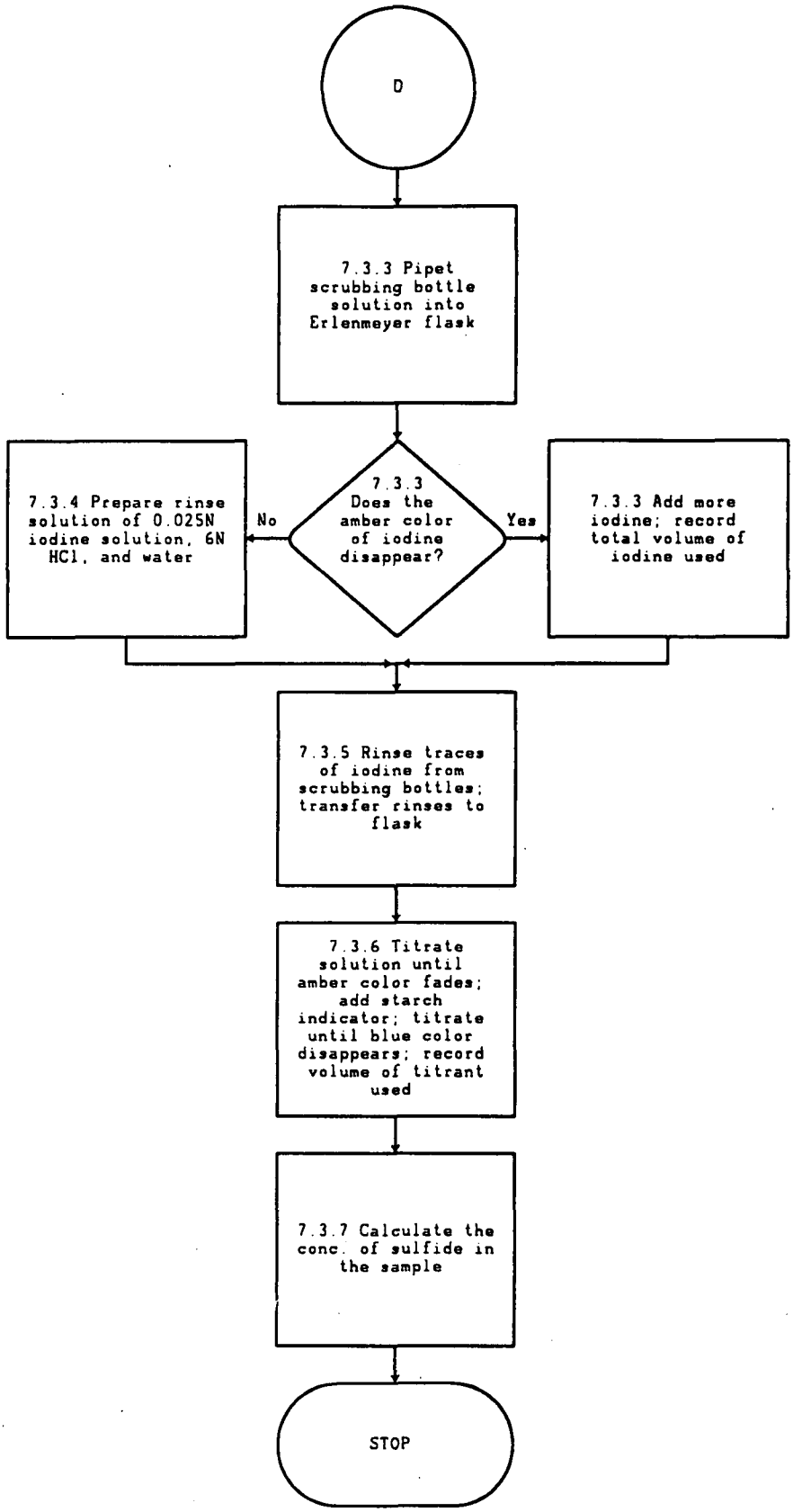


METHOD 9030A
ACID-SOLUBLE AND ACID-INSOLUBLE SULFIDES




A
7.2.1 Water content of distillation must be controlled; conc. of HCl should be 6.5N
7.2.1 Is sample easily suspended?
No
Yes
7.2.1 Limit sample size to 25 g dry weight
7.2.1 Sample size may be 25 - 50 g
7.2.2-7.2.4 Type of matrix?
Dry Solid
Moist Solid
Aqueous
7.2.2 Weigh sample; crush if necessary; add 50 mL water
7.2.4 Determine water content of sample; include total water needed for correct HCl conc.
7.2.3 Is < 50g sample needed?
No
Yes
7.2.3 Use 50 g sample
7.2.3 Add water to sample for a total volume of 50 mL
C


C
7.2.5 Place sample in flask; add stannous chloride
7.2.6 Assemble distillation apparatus; place zinc acetate/sodium acetate buffer and formaldehyde in scrubbing bottles
7.2.7 Add 100 mL 9.8N HCl to dropping funnel
7.2.8 Set nitrogen flow; purge system of oxygen for 15 mins.
7.2.9 Turn on stirrer; add HCl to distillation flask
7.2.10 Heat water bath to boil; distill for 90 mins. at 100 C; shut off nitrogen; turn off heat
7.2.11 Analyze by titration
B
7.3.1 Pipet known amount of 0.025N iodine solution in flask; bring to volume with water
7.3.2 Is acid soluble distillation being used?
No
Yes
7.3.2 Add 10 mL 6N HCl
7.3.2 Add 2 mL 6N HCl
D


D
7.3.3 Pipet scrubbing bottle solution into Erlenmeyer flask
7.3.3 Does the amber color of iodine disappear?
No
Yes
7.3.4 Prepare rinse solution of 0.025N iodine solution, 6N HCl, and water
7.3.3 Add more iodine; record total volume of iodine used
7.3.5 Rinse traces of iodine from scrubbing bottles; transfer rinses to flask
7.3.6 Titrate solution until amber color fades; add starch indicator; titrate until blue color disappears; record volume of titrant used
7.3.7 Calculate the conc. of sulfide in the sample
STOP

METHOD 9031

EXTRACTABLE SULFIDES

1.0 SCOPE AND APPLICATION

1.1 The extraction procedure described in this method is designed for the extraction of sulfides from matrices that are not directly amenable to the distillation procedure Method 9030. Specifically, this method is designed for the extraction of soluble sulfides. This method is applicable to oil, solid, multiphasic, and all other matrices not amenable to analysis by Method 9030. This method is not applicable for reactive sulfide. Refer to Chapter Seven for the determination of reactive sulfide.

1.2 Method 9031 is suitable for measuring sulfide in solid samples at concentrations above 1 mg/kg.

2.0 SUMMARY OF METHOD

2.1 If the sample contains solids that will interfere with agitation and homogenization of the sample mixture, or so much oil or grease as to interfere with the formation of a homogeneous emulsion in the distillation procedure, the sample may be filtered and the solids extracted with water at pH > 9 and < 11. The extract is then combined with the filtrate and analyzed by the distillation procedure. Separation of sulfide from the sample matrix is accomplished by the addition of sulfuric acid to the sample. The sample is heated to 70°C and the hydrogen sulfide (H_2S) which is formed is distilled under acidic conditions and carried by a nitrogen stream into zinc acetate gas scrubbing bottles where it is precipitated as zinc sulfide.

2.2 The sulfide in the zinc sulfide precipitate is oxidized to sulfur with a known amount of excess iodine. Then the excess iodine is determined by titration with a standard solution of phenylarsine oxide (PAO) or sodium thiosulfate until the blue iodine starch complex disappears. The use of standard sulfide solutions is not possible because of their instability to oxidative degradation. Therefore quantitation is based on the PAO or sodium thiosulfate.

3.0 INTERFERENCES

3.1 Samples with aqueous layers must be taken with a minimum of aeration to avoid volatilization of sulfide or reaction with oxygen which oxidizes sulfide to sulfur compounds that are not detected.

3.2 Sulfur compounds such as sulfite and hydrosulfite decompose in acid and may form sulfur dioxide. This gas may be carried over to the zinc acetate gas scrubbing bottles and subsequently react with the iodine solution yielding false high values. The addition of formaldehyde into the zinc acetate gas scrubbing bottles removes this interference. Any sulfur dioxide entering the scrubber will form an addition compound with the formaldehyde which is unreactive towards the iodine in the acidified mixture. This method shows no sensitivity to sulfite or hydrosulfite at concentrations up to 10 mg/kg of the interferant.

3.3 The iodometric method suffers interference from reducing substances that react with iodine including thiosulfate, sulfite, and various organic compounds.

3.4 Interferences have been observed when analyzing samples with high metal content such as electroplating waste and chromium containing tannery waste.

4.0 APPARATUS AND MATERIALS

4.1 Extractor - Any suitable device that sufficiently agitates a sealed container of one liter volume or greater. For the purpose of this analysis, agitation is sufficient when:

1. All sample surfaces are continuously brought into contact with extraction fluid, and

2. The agitation prevents stratification of the sample and fluid.

Examples of suitable extractors are shown in Figures 2 and 3. The tumble-extractors turn the extraction bottles end-over-end at a rate of about 30 rpm. The apparatus in Figure 2 may be easily fabricated from plywood. The jar compartments must be padded with polyurethane foam to absorb shock. The drive apparatus is a Norton jar mill.

4.2 Buchner funnel apparatus

4.2.1 Buchner funnel - 500-mL capacity, with 1-liter vacuum filtration flask.

4.2.2 Glass wool - Suitable for filtering, 0.8 m diameter such as Corning Pyrex 3950.

4.2.3 Vacuum source - Preferably a water driven aspirator. A valve or stopcock to release vacuum is required.

4.3 Gas Evolution apparatus as shown in Figure 1

4.3.1 Three neck flask - 500-mL, 24/40 standard tapered joints.

4.3.2 Dropping funnel - 100-mL, 24/40 outlet joint.

4.3.3 Purge gas inlet tube - 24/40 joint with course frit.

4.3.4 Purge gas outlet - 24/40 joint reduced to 1/4 inch tube.

4.3.5 Gas scrubbing bottles - 125-mL, with 1/4 in. o.d. inlet and outlet tubes. Impinger tube must not be fritted.

4.3.6 Tubing - 1/4 in. o.d. Teflon or polypropylene. Do not use rubber.

4.4 Hot plate stirrer.

4.5 pH meter.

4.6 Nitrogen regulator.

4.7 Flowmeter.

4.8 Separatory funnels - 500-mL.

4.9 Tumbler - See Figures 2 and 3.

4.10 Top-loading balance - capable of weighing 0.1 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Zinc acetate (for sample preservation) (2N), $Zn(CH_3COO)_2 \cdot 2H_2O$. Dissolve 220 g of zinc acetate dihydrate in 500 mL of water.

5.4 Sodium hydroxide (50% w/v in water), NaOH. Commercially available.

5.5 Tin (II) chloride, $SnCl_2 \cdot 2H_2O$, granular.

5.6 n-Hexane, C_6H_{14}.

5.7 Nitrogen, N_2.

5.8 Sulfuric acid (concentrated), H_2SO_4.

5.9 Zinc acetate for the scrubber (approximately 0.5M). Dissolve 110 g zinc acetate dihydrate in 200 mL of water. Add 1 mL concentrated hydrochloric acid, HCl, to prevent precipitation of zinc hydroxide. Dilute to 1 liter.

5.10 Formaldehyde (37% solution), CH_2O. Commercially available.

5.11 Starch solution. Use either an aqueous solution or soluble starch powder mixtures. Prepare an aqueous solution as follows. Dissolve 2 g soluble starch and 2 g salicylic acid, $C_7H_6O_3$, as a preservative, in 100 mL hot water.

5.12 Iodine solution (approximately 0.025N). Dissolve 25 g of potassium iodide, KI, in 700 mL of water in a 1-liter volumetric flask. Add 3.2 g of iodine, I_2. Allow to dissolve. Dilute to 1 liter and standardize as follows. Dissolve approximately 2 g KI in 150 mL of water. Pipet exactly 20 mL of the iodine solution to be titrated and dilute to 300 mL with water. Titrate with 0.025N standard phenylarsine oxide, or 0.025N sodium thiosulfate, $Na_2S_2O_3$, until the amber color fades. Add starch indicator solution until the solution turns

deep blue. Continue titration drop by drop until the blue color disappears. Run in replicate. Calculate the normality as follows:

$$\text{Normality } (I_2) = \frac{\text{mL of titrant x normality of titrant}}{\text{Volume of sample (mL)}}$$

5.13 Sodium sulfide nonanhydrate $Na_2S \cdot 9H_2O$, for the preparation of standard solutions to be used for calibration curves. Standards must be prepared at pH > 9 and < 11.

5.14 Titrant.

5.14.1 Standard phenylarsine oxide (PAO) solution (0.025N), C_6H_5AsO. This solution is commercially available.

CAUTION: PAO is toxic.

5.14.2 Standard sodium thiosulfate solution (0.025N), $Na_2S_2O_3 \cdot 5H_2O$. Dissolve 6.205 $\pm$ 0.005 g $Na_2S_2O_3 \cdot 5H_2O$ in 500 mL of water. Add 9 mL 1N NaOH and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All samples must be preserved with zinc acetate and sodium hydroxide. Use four drops of 2N zinc acetate solution per 100 mL of aqueous or multiphasic sample. Adjust the pH to greater than 9.0 with 50% NaOH. Fill the sample bottle completely and stopper with a minimum of aeration. For solid samples, fill the surface of solid with 2N zinc acetate until moistened. Samples must be cooled to 4°C during storage.

7.0 PROCEDURE

7.1 Assemble the Buchner funnel apparatus. Unroll the glass wool and fold the fiber over itself several times to make a pad about 1 cm thick when lightly compressed. Cut the pad to fit the Buchner funnel. Dry and weigh the pad, then place it in the funnel. Turn on the aspirator and wet the pad with a known amount of water.

7.2 Transfer a sample that contains between 1 and 50 mg of sulfide to the Buchner funnel. Rinse the sample container with known amounts of water and add the rinses to the Buchner funnel. When no free water remains in the funnel, slowly open the stopcock to allow air to enter the vacuum flask. A small amount of sediment may have passed through the glass fiber pad. This will not interfere with the analysis.

7.3 Transfer the solid and the glass fiber pad to a dried tared weighing dish. Since most greases and oils will not pass through the fiber pad, solids, oils, and greases will be extracted together. If the filtrate includes an oil phase, transfer the filtrate to a separatory funnel. Collect and measure the volume of the aqueous phase. Transfer the oil phase to the weighing dish with the solid and glass fiber pad.

7.4 Weigh the dish containing solid, oil (if any), and glass fiber pad. Subtract the weight of the dry glass fiber pad. Calculate the volume of water present in the original sample by subtracting the total volume of rinses from the measured volume of the filtrate.

7.5 Place the following in a 1-liter wide-mouth bottle:

500 mL water
5 mL 50% w/v NaOH
1 g $SnCl_2 \cdot 2H_2O$
50 mL n-hexane (if an oil or grease is present).

Cap the bottle with a Teflon or polyethylene lined cap and shake vigorously to saturate the solution with stannous chloride. Direct a stream of nitrogen gas at about 10 mL/min into the bottle for about 1 minute to purge the headspace of oxygen. If the weight of the solids (Step 7.4) is greater than 25 g, weigh out a representative aliquot of 25 g and add it to the bottle while still purging with nitrogen. Otherwise, add all of the solids. Cap the bottle; avoid the influx of air.

7.6 The pH of the extract must be maintained at > 9 or < 11 throughout the extraction step and subsequent filtration. Since some samples may release acid, the pH must be monitored as follows. Shake the extraction bottle and wait 1 minute. Open the bottle under a stream of nitrogen and check the pH. If the pH is below 9, add 50% NaOH in 5 mL increments until it is at least 9. Recap the bottle, and repeat the procedure until the pH does not drop. The bottle must be thoroughly purged of oxygen before each recapping. Oxygen will oxidize sulfide to elemental sulfur or other sulfur containing compounds that will not be detected.

7.7 Place the bottle in the tumbler, making sure there is enough foam insulation to cushion the bottle. Turn the tumbler on and allow the extraction to run for about 18 hours.

7.8 Prepare a Buchner funnel apparatus as in Step 7.1 with a glass fiber pad filter.

7.9 Decant the extract to the Buchner funnel.

7.10 If the extract contains an oil phase, separate the aqueous phase using a separatory funnel. Neither the separation nor the filtration are critical, but are necessary to be able to measure the volume of the aqueous extract analyzed. Small amounts of suspended solids and oil emulsions will not interfere with the extraction.

7.11 At this point, an aliquot of the filtrate of the original sample may be combined with an aliquot of the extract in a proportion representative of the sample. Calculate the proportions as follows:

$$\frac{\text{Aliquot of the Filtrate(mL)}}{\text{Aliquot of the Extract(mL)}} = \frac{\text{Solid Extracted(g)}^a}{\text{Total Solid(g)}^b} \times \frac{\text{Total Sample Filtrate(mL)}^c}{\text{Total Extraction Fluid(mL)}^d}$$

[a]From Step 7.5. Weight of solid sample used for extraction.

[b]From Step 7.4. Weight of solids and oil phase with the dry weight of filter and tared dish subtracted.

[c]Includes volume of all rinses added to the filtrate (Steps 7.1 and 7.2).

[d]500 mL water plus total volume of NaOH solution. Does not include hexane, which is subsequently removed (Step 7.10).

Alternatively, the samples may be distilled and analyzed separately, concentrations for each phase reported separately, and the amounts of each phase present in the sample reported separately.

7.12 Distillation of Sulfide

7.12.1 In a preliminary experiment, determine the approximate amount of sulfuric acid required to adjust a measured amount of the sample to pH less than or equal to 1. The sample size should be chosen so that it contains between 1.0 and 50 mg of sulfide. Place a known amount of sample or sample slurry in a beaker. Add water until the total volume is 200 mL. Stir the mixture and determine the pH. Slowly add sulfuric acid until the pH is less than or equal to 1.

CAUTION: Toxic hydrogen sulfide may be generated from the acidified sample. This operation must be performed in the hood and the sample left in the hood until the sample has been made alkaline or the sulfide has been destroyed.

From the amount of sulfuric acid required to acidify the sample and the mass or volume of the sample acidified, calculate the amount of acid required to acidify the sample to be placed in the distillation flask.

7.12.2 Prepare the gas evolution apparatus as shown in Figure 1 in a fume hood.

7.12.2.1 Prepare a hot water bath at 70°C by filling a crystallizing dish or other suitable container with water and place it on a hotplate stirrer. Place a thermometer in the bath and monitor the temperature to maintain the bath at 70°C.

7.12.2.2 Assemble the three neck 500-mL flask, fritted gas inlet tube, and exhaust tube. Use Teflon sleeves to seal the ground glass joints. Place a Teflon coated stirring bar into the flask.

7.12.2.3 Place into each gas scrubbing bottle 10 $\pm$ 0.5 mL of the 0.5M zinc acetate solution, 5.0 $\pm$ 0.1 mL of 37% formaldehyde and 100 $\pm$ 5.0 mL water.

7.12.2.4 Connect the gas evolution flask and gas scrubbing bottles as shown in Figure 1. Secure all fittings and joints.

7.12.3 Carefully place an accurately weighed sample which contains 1.0 to 50 mg of sulfide into the flask. If necessary, dilute to approximately 200 mL with water.

7.12.4 Place the dropping funnel onto the flask making sure its stopcock is closed. Add the volume of sulfuric acid calculated in Step 7.1.1 plus an additional 50 mL into the dropping funnel. The bottom stopcock must be closed.

7.12.5 Attach the nitrogen inlet to the top of the dropping funnel gas shut-off valve. Turn on the nitrogen purge gas and adjust the flow through the sample flask to 25 mL/min. The nitrogen in the gas scrubbing bottles should bubble at a rate of about five bubbles per second. Nitrogen pressure should be limited to approximately 10 psi to prevent excess stress on the glass system and fittings. Verify that there are no leaks in the system. Open the nitrogen shut-off valve leading to the dropping funnel. Observe that the gas flow into the sample vessel will stop for a short period while the pressure throughout the system equalizes. If the gas flow through the sample flask does not return within a minute, check for leaks around the dropping funnel. Once flow has stabilized, turn on the magnetic stirrer. Purge the system for 15 minutes with nitrogen to remove oxygen.

7.12.6 Heat sample to 70°C. Open dropping funnel to a position that will allow a flow of sulfuric acid of approximately 5 mL/min. Monitor the system until most of the sulfuric acid contained within the dropping funnel has entered the sample flask. Close the dropping funnel while a small amount of acid remains. Immediately close the gas shut-off valve to the dropping funnel.

7.12.7 Purge, stir, and maintain a temperature of 70°C for a total of 90 minutes from start to finish. Shut off nitrogen supply. Turn off heat.

7.13 Titration of Distillate

7.13.1 Pipet a known amount of standardized 0.025N iodine solution (see Step 5.12) in a 500-mL flask, adding an amount in excess of that needed to oxidize the sulfide. Add enough water to bring the volume to 100 mL. The volume of standardized iodine solution should be about 65 mL for samples with 50 mg of sulfide.

7.13.2 Add 2 mL of 6N HCl to the iodine.

7.13.3 Pipet both of the gas scrubbing bottle solutions into the flask, keeping the end of the pipet below the surface of the iodine solution. If at any point in transferring the zinc acetate solution or rinsing the bottles, the amber color of the iodine disappears or fades to yellow, more 0.025N iodine must be added. This additional amount must be added to the amount from Step 7.13.1 for calculations. Record the total volume of standardized 0.025N iodine solution used.

7.13.4 Prepare a rinse solution of a known amount of standardized 0.025N iodine solution, 1 mL of 6N HCl, and water to rinse the remaining

white precipitate (zinc sulfide) from the gas scrubbing bottles into the flask. There should be no visible traces of precipitate after rinsing.

7.13.5 Rinse any remaining traces of iodine from the gas scrubbing bottles with water, and transfer the rinses to the flask.

7.13.6 Titrate the solution in the flask with standard 0.025N phenylarsine oxide or 0.025N sodium thiosulfate solution until the amber color fades to yellow. Add enough starch indicator for the solution to turn dark blue and titrate until the blue disappears. Record the volume of titrant used.

7.13.7 Calculate the concentration of sulfide in the sample as follows:

$$\frac{[(\text{mL of } I_2 \times \text{N of } I_2) - (\text{mL of titrant} \times \text{N of titrant})](16.03)}{\text{sample weight (kg)}} = \text{sulfide(mg/kg)}$$

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by or under supervision of experienced analysts. Refer to the appropriate section of Chapter One for additional quality control requirements.

8.2 A reagent blank should be run every twenty analyses or per analytical batch, whichever is more frequent.

8.3 Check standards are prepared from water and a known amount of sodium sulfide. A check standard should be run with each analytical batch of samples or once every twenty samples. Acceptable recovery will depend on the level and matrix.

8.4 A matrix spiked sample should be run for each analytical batch or twenty samples, whichever is more frequent, to determine matrix effects. If recovery is low, acid-insoluble sulfides are indicated. A matrix spiked sample is a sample brought through the whole sample preparation and analytical process.

8.5 Verify the calibration with an independently prepared QC reference sample every twenty samples or once per analytical batch, whichever is more frequent.

9.0 METHOD PERFORMANCE

9.1 Accuracy - Accuracy for this method was determined by three independent laboratories by measuring percent recoveries of spikes for waste samples. The results are summarized below.

Accuracy for the entire method for four synthetic waste samples 70-104% recovery

9.2 Precision

Precision of entire method for four synthetic waste samples
Percent coefficient of variation 1.0-34

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FIGURE 1.
GAS EVOLUTION APPARATUS

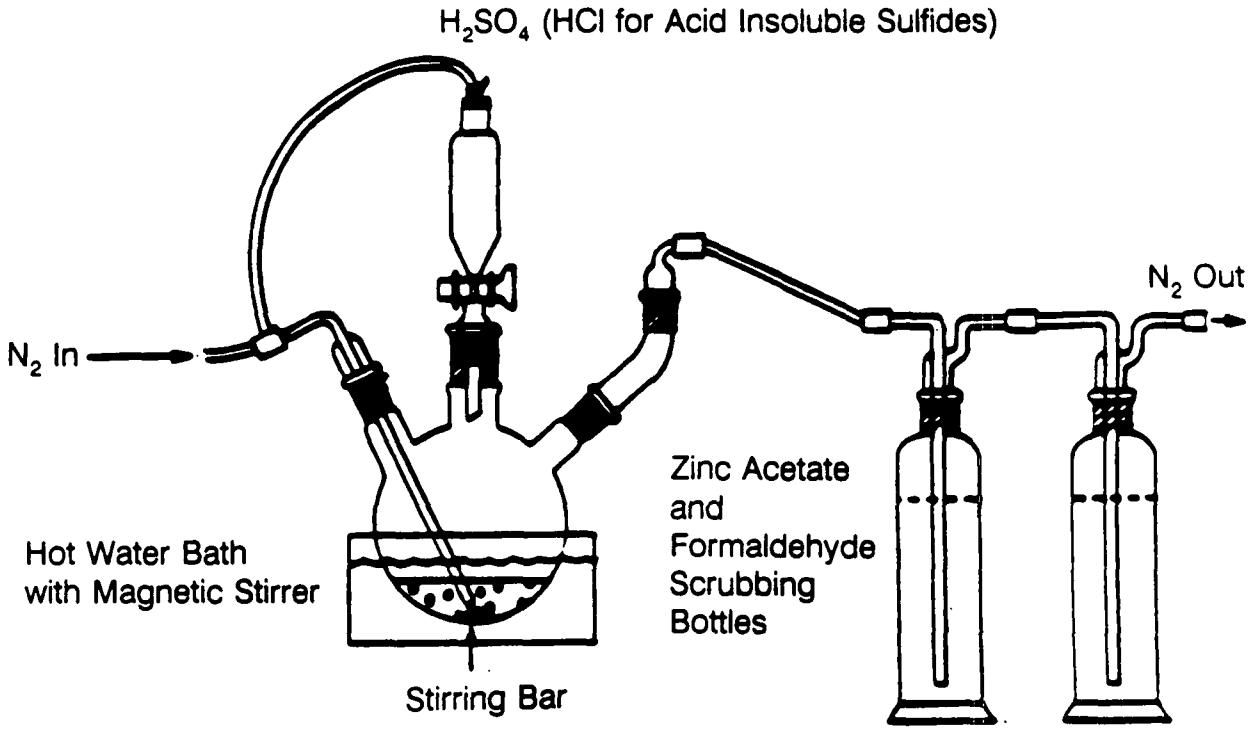


FIGURE 2.
TUMBLER-EXTRACTOR

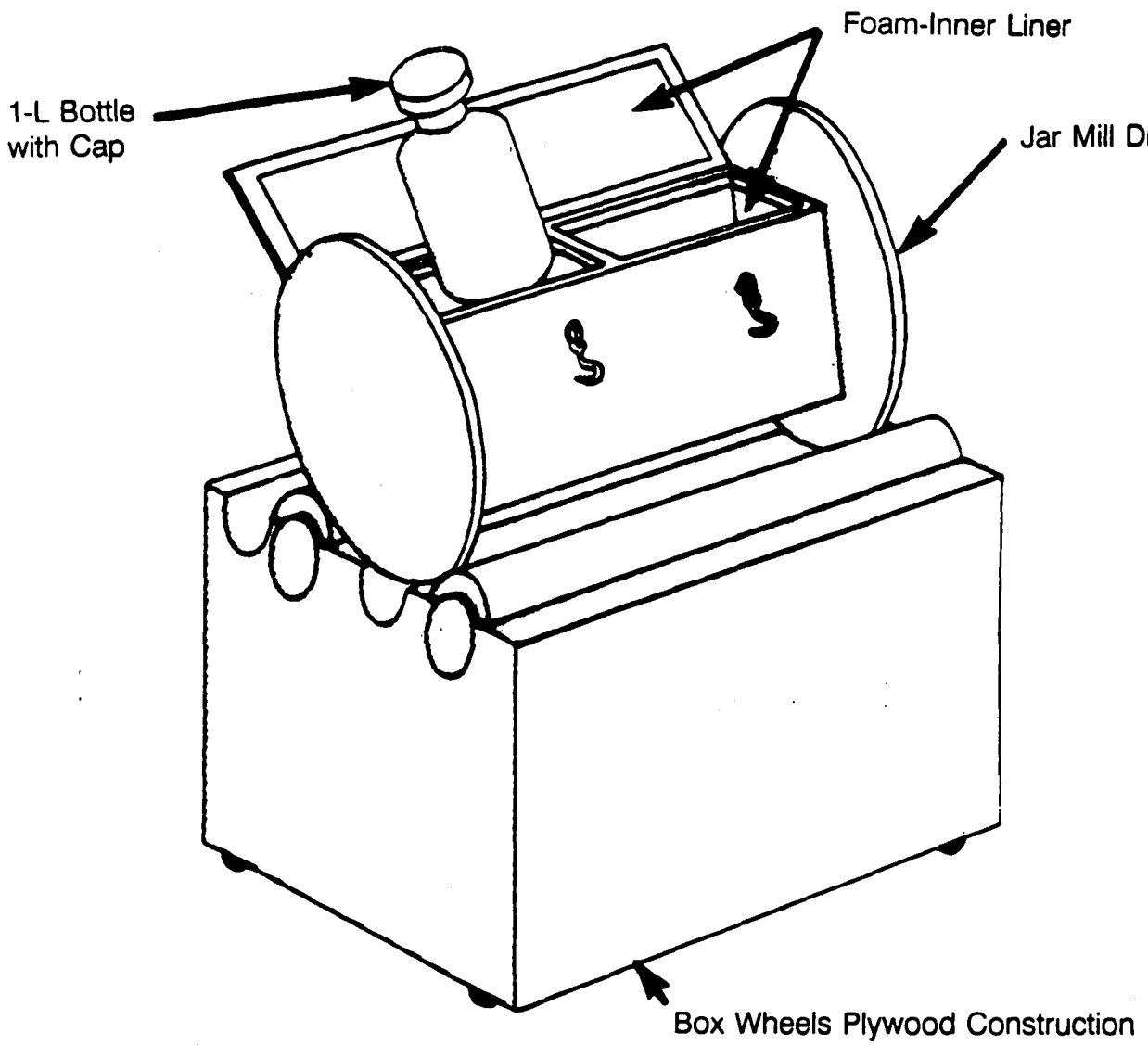
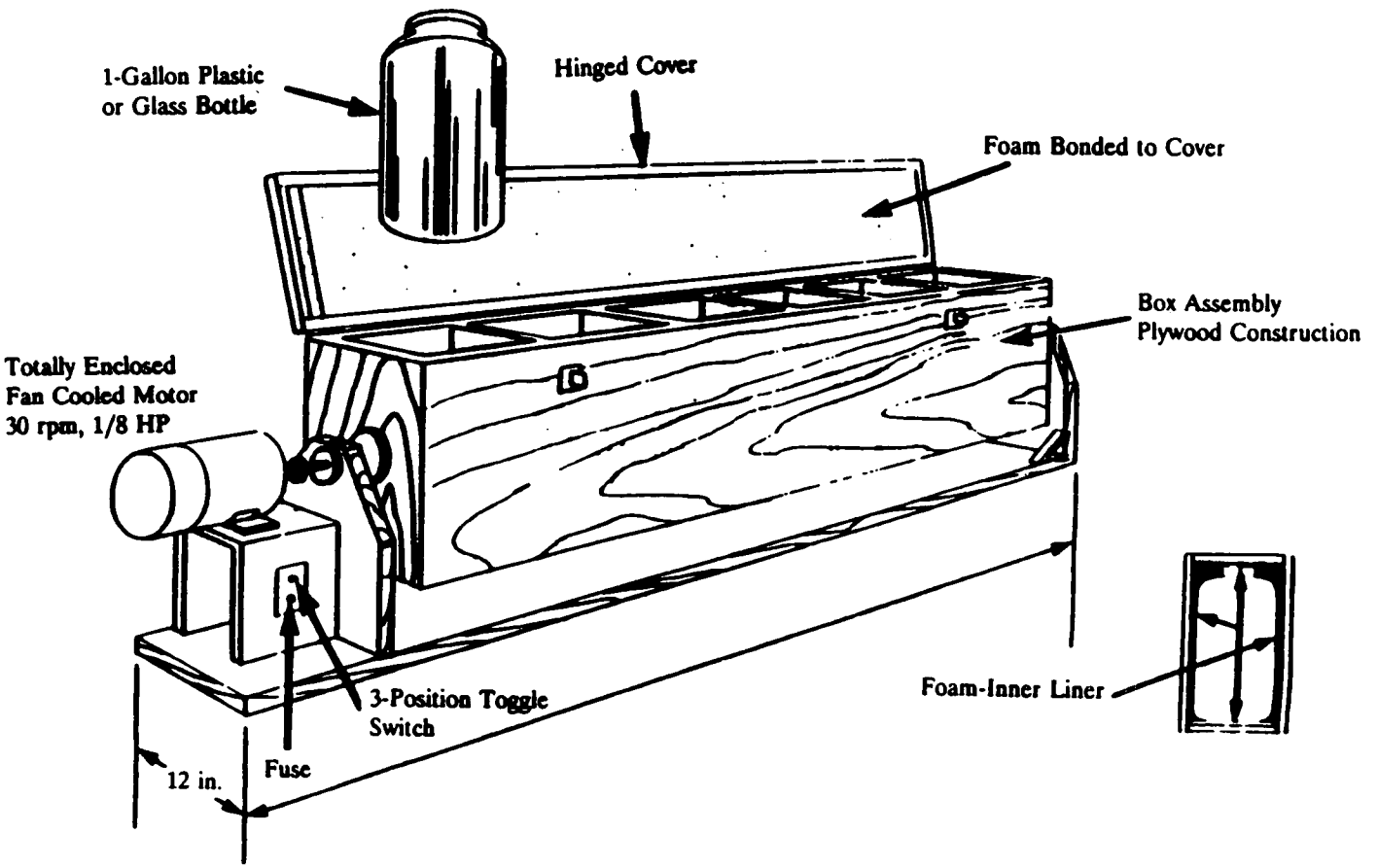
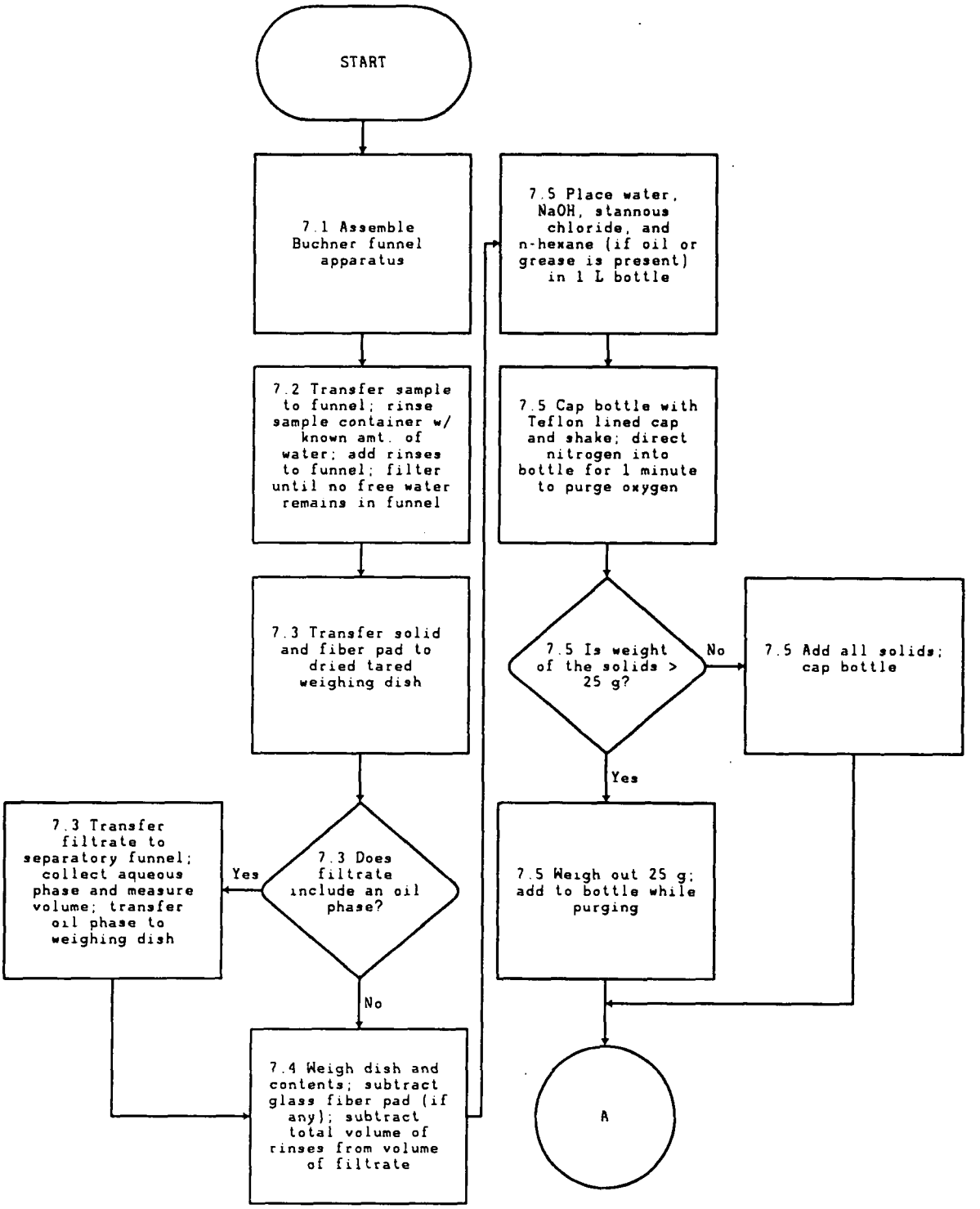
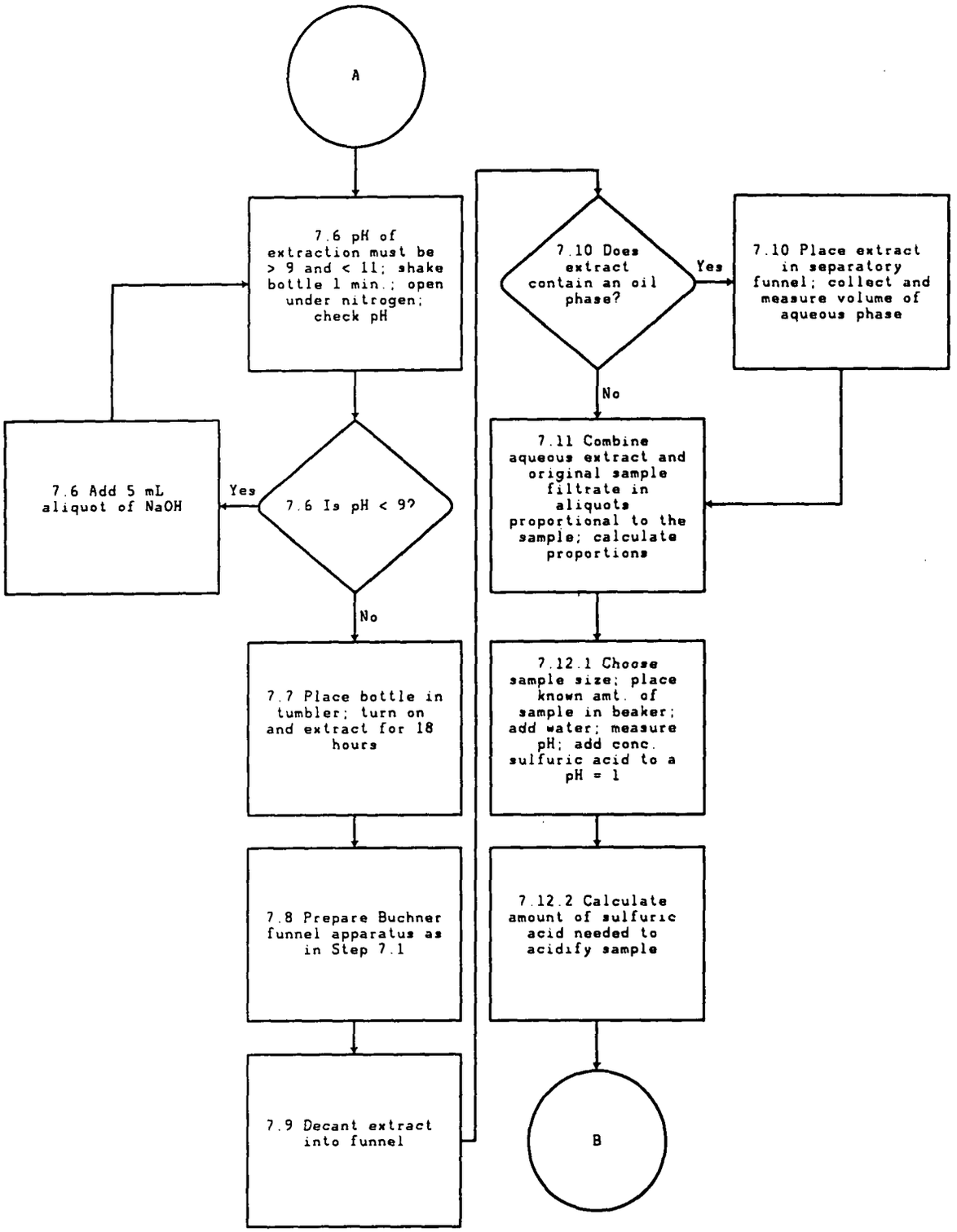
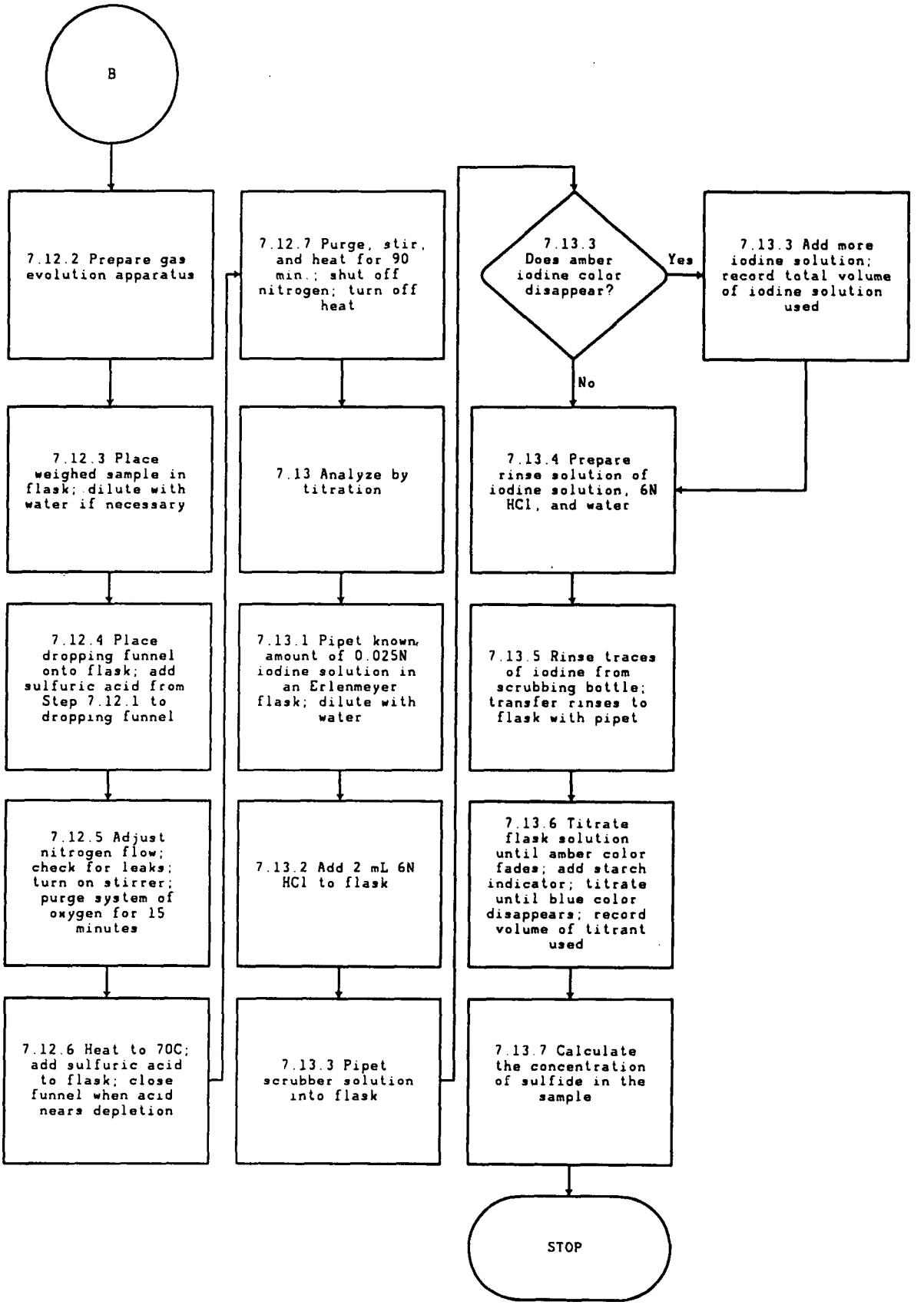


FIGURE 3.
EXTRACTOR




START
7.1 Assemble Buchner funnel apparatus
7.2 Transfer sample to funnel; rinse sample container w/ known amt. of water; add rinses to funnel; filter until no free water remains in funnel
7.3 Transfer solid and fiber pad to dried tared weighing dish
7.3 Does filtrate include an oil phase?
Yes
7.3 Transfer filtrate to separatory funnel; collect aqueous phase and measure volume; transfer oil phase to weighing dish
No
7.4 Weigh dish and contents; subtract glass fiber pad (if any); subtract total volume of rinses from volume of filtrate
7.5 Place water, NaOH, stannous chloride, and n-hexane (if oil or grease is present) in 1 L bottle
7.5 Cap bottle with Teflon lined cap and shake; direct nitrogen into bottle for 1 minute to purge oxygen
7.5 Is weight of the solids > 25 g?
No
7.5 Add all solids; cap bottle
Yes
7.5 Weigh out 25 g; add to bottle while purging
A


A
7.6 pH of extraction must be > 9 and < 11; shake bottle 1 min.; open under nitrogen; check pH
7.6 Is pH < 9?
Yes
7.6 Add 5 mL aliquot of NaOH
No
7.7 Place bottle in tumbler; turn on and extract for 18 hours
7.8 Prepare Buchner funnel apparatus as in Step 7.1
7.9 Decant extract into funnel
7.10 Does extract contain an oil phase?
Yes
7.10 Place extract in separatory funnel; collect and measure volume of aqueous phase
No
7.11 Combine aqueous extract and original sample filtrate in aliquots proportional to the sample; calculate proportions
7.12.1 Choose sample size; place known amt. of sample in beaker; add water; measure pH; add conc. sulfuric acid to a pH = 1
7.12.2 Calculate amount of sulfuric acid needed to acidify sample
B


B
7.12.2 Prepare gas evolution apparatus
7.12.3 Place weighed sample in flask; dilute with water if necessary
7.12.4 Place dropping funnel onto flask; add sulfuric acid from Step 7.12.1 to dropping funnel
7.12.5 Adjust nitrogen flow; check for leaks; turn on stirrer; purge system of oxygen for 15 minutes
7.12.6 Heat to 70C; add sulfuric acid to flask; close funnel when acid nears depletion
7.12.7 Purge, stir, and heat for 90 min.; shut off nitrogen; turn off heat
7.13 Analyze by titration
7.13.1 Pipet known amount of 0.025N iodine solution in an Erlenmeyer flask; dilute with water
7.13.2 Add 2 mL 6N HCl to flask
7.13.3 Pipet scrubber solution into flask
7.13.3 Does amber iodine color disappear?
Yes
7.13.3 Add more iodine solution; record total volume of iodine solution used
No
7.13.4 Prepare rinse solution of iodine solution, 6N HCl, and water
7.13.5 Rinse traces of iodine from scrubbing bottle; transfer rinses to flask with pipet
7.13.6 Titrate flask solution until amber color fades; add starch indicator; titrate until blue color disappears; record volume of titrant used
7.13.7 Calculate the concentration of sulfide in the sample
STOP

METHOD 9035

SULFATE (COLORIMETRIC, AUTOMATED, CHLORANILATE)

1.0 SCOPE AND APPLICATION

1.1 This automated method is applicable to ground water, drinking and surface waters, and domestic and industrial wastes containing 10 to 400 mg SO_4^{-2}/liter.

2.0 SUMMARY OF METHOD

2.1 When solid barium chloranilate is added to a solution containing sulfate, barium sulfate is precipitated, releasing the highly colored acid chloranilate ion. The color intensity in the resulting chloranilic acid solution is proportional to the amount of sulfate present.

3.0 INTERFERENCES

3.1 Cations such as calcium, aluminum, and iron interfere by precipitating the chloranilate. These ions are removed by passage through an ion-exchange column.

3.2 Samples should be centrifuged or filtered before analysis.

4.0 APPARATUS AND MATERIALS

4.1 Automated continuous-flow analytical instrument, with:

4.1.1 Sampler I.

4.1.2 Continuous filter.

4.1.3 Manifold.

4.1.4 Proportioning pump.

4.1.5 Colorimeter: Equipped with 15 mm tubular flowcell and 520 nm filters.

4.1.6 Recorder.

4.1.7 Heating bath, 45°C.

4.2 Magnetic stirrer.

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5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Barium chloranilate: Add 9 g of barium chloranilate ($BaC_6Cl_2O_4$) to 333 mL of spectrophotometric grade ethyl alcohol and dilute to 1 liter with Type II water.

5.3 Acetate buffer, pH 4.63: Dissolve 13.6 g of sodium acetate in Type II water. Add 6.4 mL of acetic acid and dilute to 1 liter with Type II water. Make fresh weekly.

5.4 NaOH-EDTA solution: Dissolve 65 g of NaOH and 6 g EDTA in Type II water and dilute to 1 liter. This solution is also used to clean out the manifold system at end of sampling run.

5.5 Ion exchange resin: Dowex-50 W-X8, ionic form-H^+. The column is prepared by sucking a slurry of the resin into 12 in. of 3/16-in O.D. tubing. This may be conveniently done by using a pipet and a loose-fitting glass wool plug in the tube. The column, upon exhaustion, turns red. Ensure that air does not enter the column.

5.6 Stock solution: Dissolve 1.4790 g of oven-dried (105°C) Na_2SO_4 in Type II water and dilute to 1 liter in a volumetric flask (1.0 mL = 1.0 mg).

5.7 Standards: Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 mL with Type II water. The following dilutions are suggested.

Stock Solution (mL)	Concentration (mg/L)
1.0	10
2.0	20
4.0	40
6.0	60
8.0	80
10.0	100
15.0	150
20.0	200
30.0	300
40.0	400

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Refrigerate at 4°C.

7.0 PROCEDURE

7.1 Set up manifold as shown in Figure 1. (Note that any precipitated $BaSO_4$ and the unused barium chloranilate are removed by filtration. If any $BaSO_4$ should come through the filter, it is complexed by the NaOH-EDTA reagent.)

7.2 Allow both colorimeter and recorder to warm up for 30 min. Run a baseline with all reagents, feeding Type II water through the sample line. Adjust dark current and operative opening on colorimeter to obtain suitable baseline.

7.3 Place Type II water wash tubes in alternate openings in sampler and set sample timing at 2.0 min.

7.4 Place working standards in sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.

7.5 Switch sample line from Type II water to sampler and begin analysis.

7.6 Calculation:

7.6.1 Prepare a standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A linear calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A spike duplicate sample is a sample brought through the whole sample preparation and analytical process.

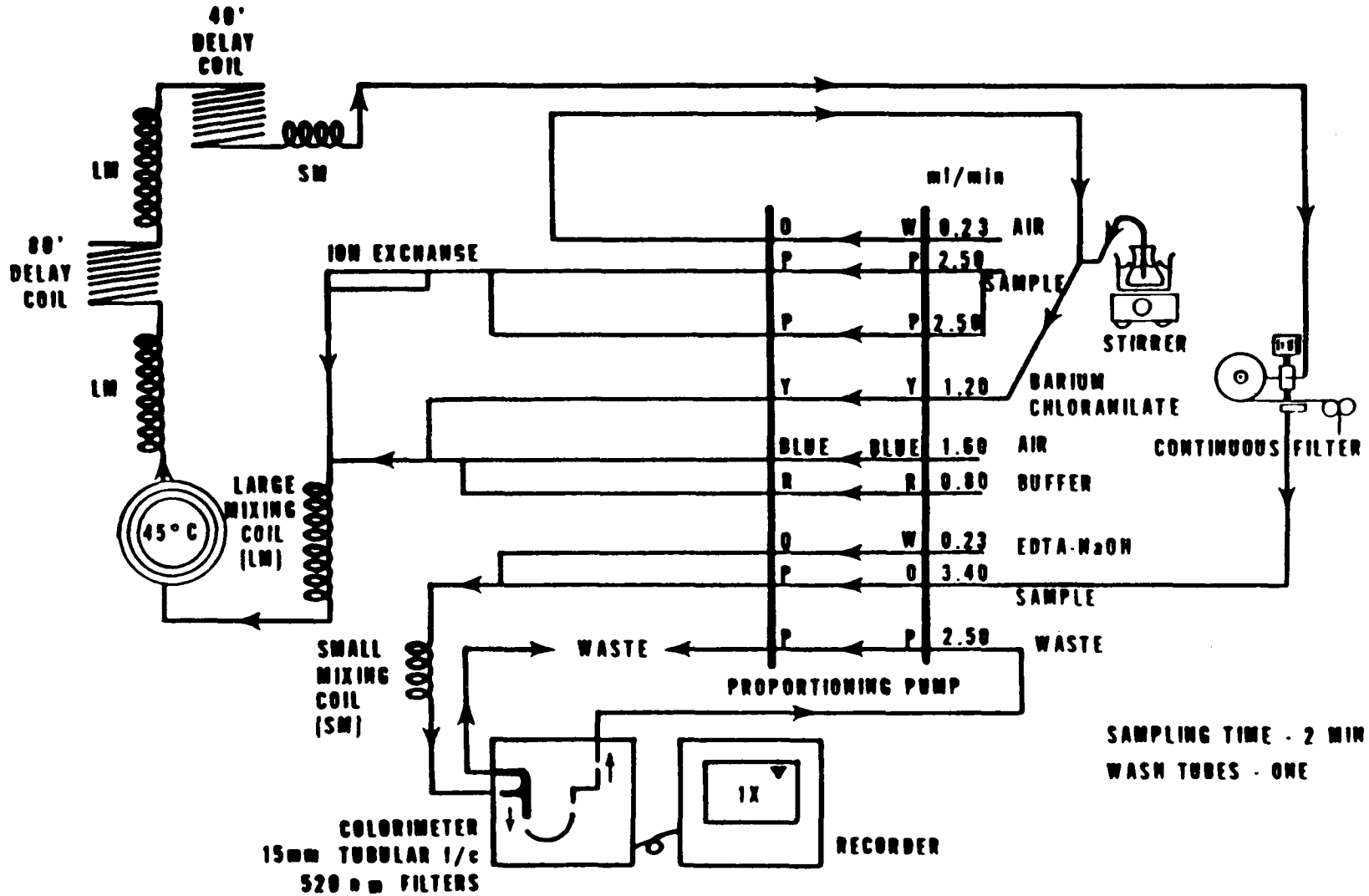

FIGURE 1 - SULFATE MANIFOLD AA-I

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9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 375.1 of Methods for Chemical Analysis of Water and Wastes.

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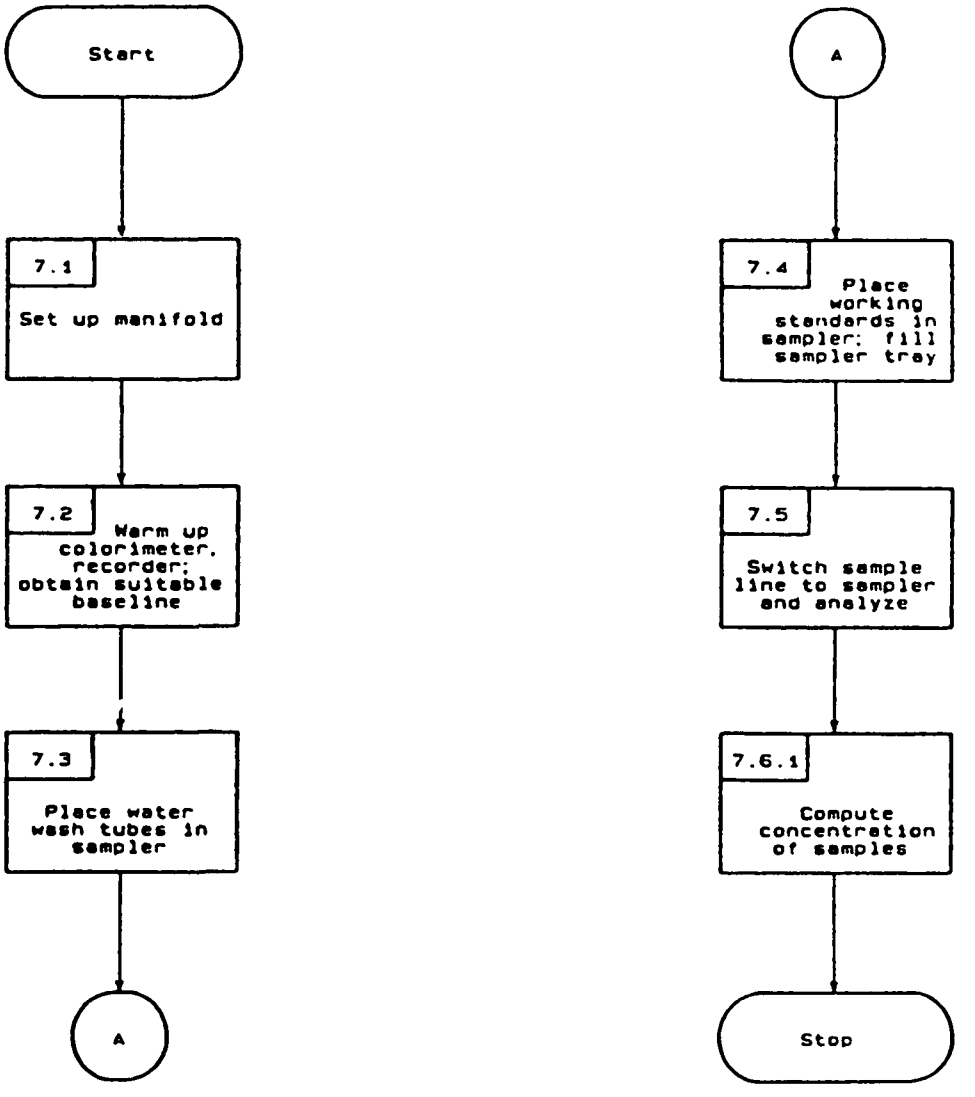

Start
7.1
Set up manifold
7.2
Warm up colorimeter, recorder; obtain suitable baseline
7.3
Place water wash tubes in sampler
A
A
7.4
Place working standards in sampler; fill sampler tray
7.5
Switch sample line to sampler and analyze
7.6.1
Compute concentration of samples
Stop

METHOD 9036

SULFATE (COLORIMETRIC, AUTOMATED, METHYLTHYMOL BLUE, AA II)

1.0 SCOPE AND APPLICATION

1.1 This automated method is applicable to ground water, drinking and surface waters, and domestic and industrial wastes.

1.2 Samples in the range of 0.5 to 300 mg SO_4^{-2}/liter can be analyzed.

2.0 SUMMARY OF METHOD

2.1 The sample is first passed through a sodium-form cation-exchange column to remove multivalent metal ions. The sample containing sulfate is then reacted with an alcohol solution of barium chloride and methylthymol blue (MTB) at a pH of 2.5-3.0 to form barium sulfate. The combined solution is raised to a pH of 12.5-13.0 so that excess barium reacts with MTB. The uncomplexed MTB color is gray; if it is all chelated with barium, the color is blue. Initially, the barium and MTB are equimolar and equivalent to 30 mg SO_4^{-2}/liter; thus the amount of uncomplexed MTB is equal to the sulfate present.

3.0 INTERFERENCES

3.1 The ion-exchange column eliminates interferences from multivalent cations. A mid-scale sulfate standard containing Ca^{++} should be analyzed periodically to ensure that the column is functioning properly.

3.2 Samples with pH below 2 should be neutralized because high acid concentrations elute cations from the ion-exchange resin.

3.3 Turbid samples should be filtered or centrifuged.

4.0 APPARATUS AND MATERIALS

4.1 Automated continuous-flow analytical instrument:

4.1.1 **Sampler.**

4.1.2 **Manifold:** High- or low-level (Figure 1).

4.1.3 **Proportioning pump.**

4.1.4 **Heating bath:** Operable at the temperature specified.

4.1.5 **Colorimeter:** Equipped with 15 mm flowcell and 460 nm interference filters.

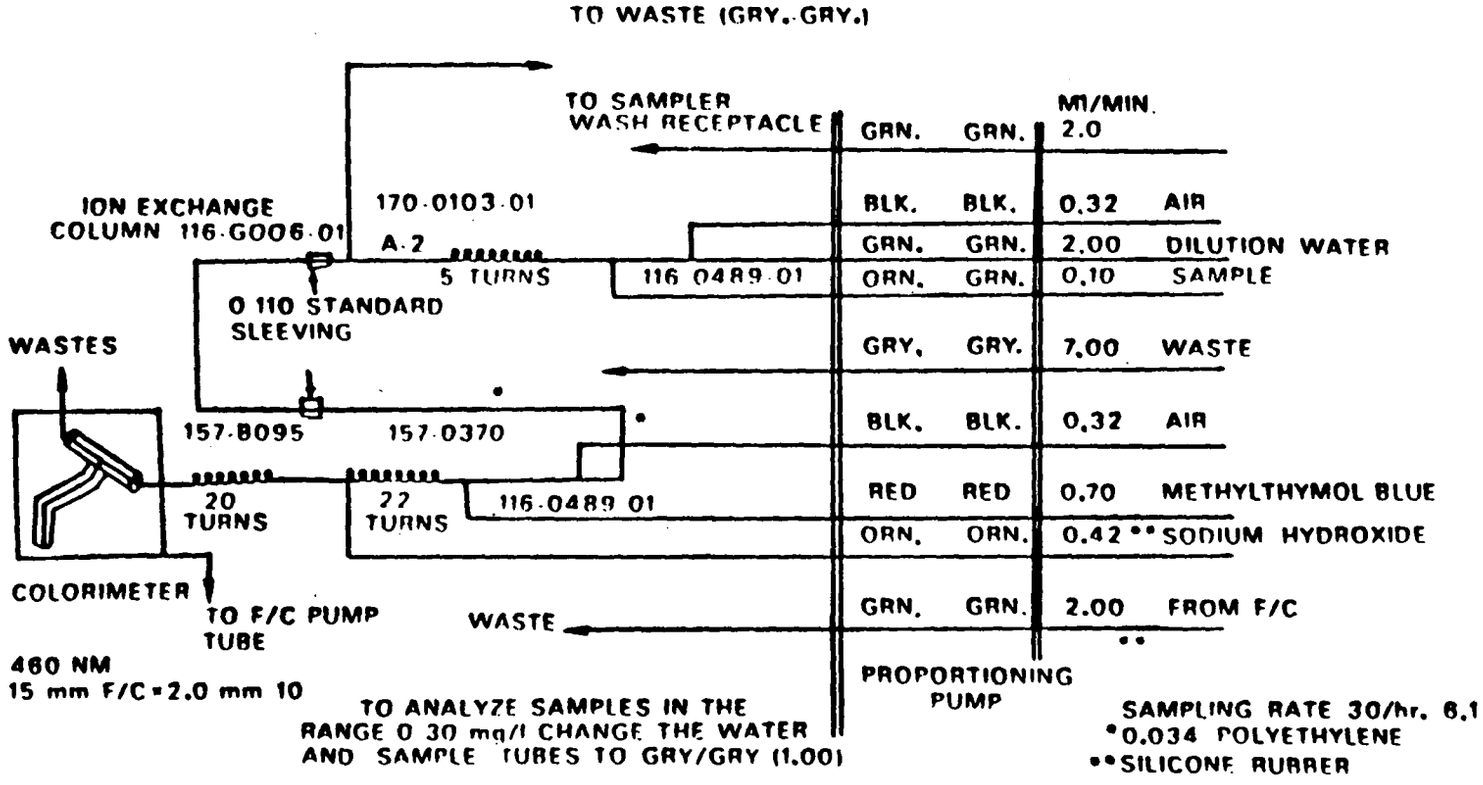


FIGURE 1 SULFATE MANIFOLD AA11

Revision 0
Date September 1986

4.1.6 **Filters:** Of specified transmittance.

4.1.7 **Recorder.**

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Barium chloride: Dissolve 1.526 g of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) in 500 mL of Type II water and dilute to 1 liter.

5.3 Methylthymol blue: Dissolve 0.1182 g of methylthymol blue (3'3"-bis-N,N-bis carboxymethyl-amino methylthymolsulfone-phthalein pentasodium salt) in 25 mL of barium chloride solution (Paragraph 5.2). Add 4 mL of 1.0 N hydrochloric acid, which changes the color to bright orange. Add 71 mL of water and dilute to 500 mL with ethanol. The pH of this solution is 2.6. This reagent should be prepared the day before and stored in a brown plastic bottle in the freezer.

5.4 Buffer, pH 10.5 ± 0.5: Dissolve 6.75 g of ammonium chloride in 500 mL of Type II water. Add 57 mL of concentrated ammonium hydroxide and dilute to 1 liter with Type II water.

5.5 Buffered EDTA: Dissolve 40 g of tetrasodium EDTA in pH 10.5 buffer (Paragraph 5.4) and dilute to 1 liter with buffer.

5.6 Sodium hydroxide solution (50%): Dissolve 500 g NaOH in 600 mL of Type II water, cool, and dilute to 1 liter.

5.7 Sodium hydroxide, 0.18 N: Dilute 14.4 mL of sodium hydroxide solution (Paragraph 5.6) to 1 liter.

5.8 Ion-exchange resin: Bio-Rex 70, 20-50 mesh, sodium form, Bio-Rad Laboratories, Richmond, California. Free from fines by stirring with several portions of Type II water and decant the supernate before settling is complete.

5.9 Dilution water: Add 0.75 mL of sulfate stock solution (Paragraph 5.10) and 3 drops of Brij-35 (available from Technicon) to 2 liters of Type II water.

5.10 Sulfate stock solution, 1 mL = 1 mg SO_4^{-2}: Dissolve 1.479 g of dried Na_2SO_4 (105°C) in Type II water and dilute to 1 liter.

5.11 Dilute sulfate solution, 1 mL = 0.1 mg SO_4^{-2}: Dilute 100 mL of sulfate stock solution (Paragraph 5.10) to 1 liter.

5.12 High-level working standards, 10-300 mg/L: Prepare high-level working standards by diluting the following volumes of stock standard (Paragraph 5.10) to 100 mL:

Stock Solution (mL)	Concentration (mg/L)
1	10
5	50
10	100
15	150
25	250
30	300

5.13 Low-level working standards, 0.5-30 mg/L: Prepare low-level working standards by diluting the following volumes of dilute sulfate solution (Paragraph 5.11) to 100 mL:

Stock Solution (mL)	Concentration (mg/L)
0.5	0.5
1	1.0
5	5.0
10	10.0
15	15.0
25	25.0
30	30.0

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Refrigerate at 4°C.

7.0 PROCEDURE

7.1 Set up manifold for high- (10-300 mg/L SO_4^{-2}) or low- (0.5-30 mg/L SO_4^{-2}) level samples as described in Figure 1.

7.2 The ion-exchange column is prepared by pulling a slurry of the resin into a piece of glass tubing 7.5-in. long, 2.0-mm I.D., and 3.6-mm O.D. This is conveniently done by using a pipet and a loose-fitting glass wool plug in the tubing. Care should be taken to avoid allowing air bubbles to enter the column. If air bubbles become trapped, the column should be prepared again. The column can exchange the equivalent of 35 mg of calcium. For the high-level manifold, this corresponds to about 900 samples with 200 mg/L Ca. The column should be prepared as often as necessary to ensure that no more than 50% of its capacity is used.

7.3 Allow the colorimeter, recorder, and printer to warm up for 30 min. Pump all reagents until a stable baseline is achieved.

7.4 Analyze all working standards in duplicate at the beginning of a run to develop a standard curve. The A and B control standards must be analyzed every hour to ensure that the system remains properly calibrated. Because the chemistry is nonlinear, the 180-mg/L standard is set at 50% on the recorder using the standard calibration control on the colorimeter.

7.5 At the end of each day, the system should be washed with the buffered EDTA solution (Paragraph 5.5). This is done by placing the methylthymol blue line and the sodium hydroxide line in water for a few minutes and then in the buffered EDTA solution for 10 min. Wash the system with water for 15 min before shutting down.

7.6 Prepare a standard curve by plotting peak heights of five processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with the standard curve. Note that this is not a linear curve but a third order curve.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

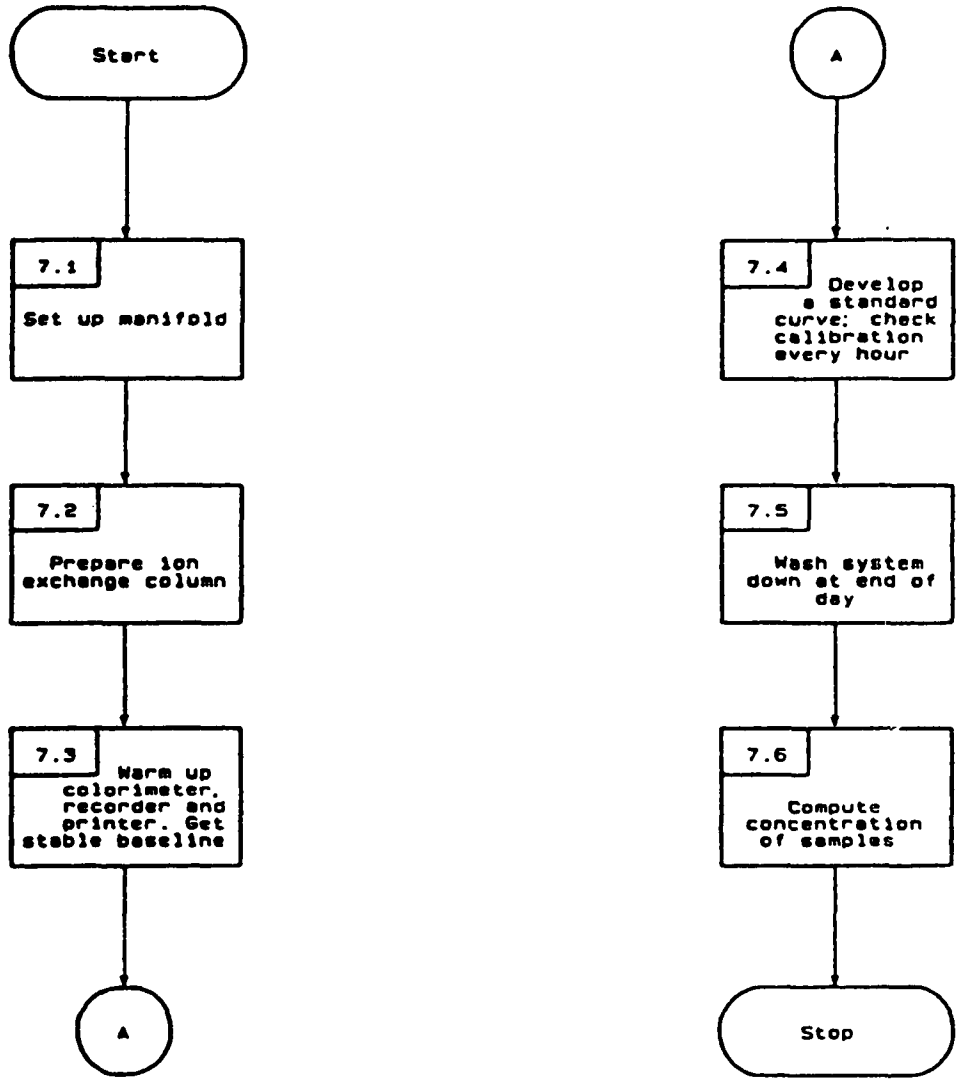
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 375.2 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Coloros, E., M.R. Panesar, and F.P. Parry, "Linearizing the Calibration Curve in Determination of Sulfate by the Methylthymol Blue Method," Anal. Chem. 48, 1693 (1976).

2. Lazrus, A.L., K.C. Hill, and J.P. Lodge, "Automation in Analytical Chemistry," Technicon Symposia, 1965.


Start
7.1
Set up manifold
7.2
Prepare ion exchange column
7.3
Warm up colorimeter, recorder and printer. Get stable baseline
A
A
7.4
Develop a standard curve; check calibration every hour
7.5
Wash system down at end of day
7.6
Compute concentration of samples
Stop

METHOD 9038

SULFATE (TURBIDIMETRIC)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to ground water, drinking and surface waters, and domestic and industrial wastes.

1.2 This method is suitable for all concentration ranges of sulfate (SO_4^{-2}); however, in order to obtain reliable readings, use a sample aliquot containing not more than 40 mg/L of SO_4^{-2}.

1.3 The minimum detectable limit is approximately 1 mg/L of SO_4^{-2}.

2.0 SUMMARY OF METHOD

2.1 Sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined by a nephelometer, filter photometer, or spectrophotometer and compared with a curve prepared from standard sulfate solution.

3.0 INTERFERENCES

3.1 Color and turbidity due to the sample matrix can cause positive interferences which must be accounted for by use of blanks.

3.2 Silica in concentrations over 500 mg/L will interfere.

4.0 APPARATUS AND MATERIALS

4.1 Magnetic stirrer: Variable speed so that it can be held constant just below splashing. Use identical shapes and sizes of magnetic stirring bars.

4.2 Photometer (one of the following, given in order of preference):

4.2.1 Nephelometer.

4.2.2 Spectrophotometer: For use at 420 nm with light path of 4 to 5 cm.

4.2.3 Filter photometer: With a violet filter having a maximum near 420 nm and a light path of 4 to 5 cm.

4.3 Stopwatch: If the magnetic stirrer is not equipped with an accurate timer.

4.4 Measuring spoon: Capacity 0.2 to 0.3 mL.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Conditioning reagent: Slowly add 30 mL concentrated HCl to 300 mL Type II water, 100 mL 95% ethanol or isopropanol, and 75 g NaCl in solution in a container. Add 50 mL glycerol and mix.b

5.3 Barium chloride ($BaCl_2$): Crystals, 20 to 30 mesh.

5.4 Sodium carbonate solution: (approximately 0.05 N): Dry 3 to 5 g primary standard Na_2CO_3 at 250°C for 4 hr and cool in a desiccator. Weigh 2.5 ± 0.2 g (to the nearest mg), transfer to a 1-liter volumetric flask, and fill to the mark with Type II water.

5.5 Proprietary reagents: Such as Hach Sulfaver or equivalent, are acceptable.

5.6 Standard sulfate solution (1.00 mL = 100 ug SO_4^{-2}): Prepare by Paragraph 5.6.1 or 5.6.2.

5.6.1 Standard sulfate solution from H_2SO_4:

5.6.1.1 Standard sulfuric acid, 0.1 N: Dilute 3.0 mL concentrated H_2SO_4 to 1 liter with Type II water. Standardize against 40.0 mL of 0.05 N Na_2CO_3 solution (Paragraph 5.4) with about 60 mL Type II water by titrating potentiometrically to a pH of about 5. Lift electrodes and rinse into beaker. Boil gently for 3 to 5 min under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate the normality of H_2SO_4 using:

$$N = \frac{A \times B}{53.00 \times C}$$

where:

A = g Na_2CO_3 weighed into 1 liter flask (Paragraph 5.4);

B = mL Na_2CO_3 solution used in the standardization;

C = mL acid used in titration;

5.6.1.2 Standard acid, 0.02 N: Dilute appropriate amount of standard acid, 0.1 N (Paragraph 5.6.1.1) to 1 liter (use 200.00 mL standard acid if normality is 0.1000 N). Check by standardization against 15 mL of 0.05 N Na_2CO_3 solution (Paragraph 5.4).

5.6.1.3 Place 10 mL standard sulfuric acid, 0.02 N (Paragraph 5.6.1.2) in a 100-mL volumetric flask and dilute to the mark.

5.6.2 **Standard sulfate solution from Na_2SO_4:** Dissolve 147.9 mg anhydrous Na_2SO_4 in Type II water in a 1-liter volumetric flask and dilute to the mark with Type II water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Preserve by refrigerating at 4°C.

7.0 PROCEDURE

7.1 Formation of barium sulfate turbidity:

7.1.1 Place a 100-mL sample, or a suitable portion diluted to 100 mL, into a 250-mL Erlenmeyer flask.

7.1.2 Add exactly 5.0 mL conditioning reagent (Paragraph 5.2).

7.1.3 Mix in the stirring apparatus.

7.1.4 While the solution is being stirred, add a measured spoonful of $BaCl_2$ crystals (Paragraph 5.3) and begin timing immediately.

7.1.5 Stir exactly 1.0 min at constant speed.

7.2 Measurement of barium sulfate turbidity:

7.2.1 Immediately after the stirring period has ended, pour solution into absorbance cell.

7.2.2 Measure turbidity at 30-sec intervals for 4 min.

7.2.3 Record the maximum reading obtained in the 4-min period.

7.3 Preparation of calibration curve:

7.3.1 Prepare calibration curve using standard sulfate solution (Paragraph 5.6).

7.3.2 Space standards at 5-mg/L increments in the 0-40 mg/L sulfate range.

7.3.3 Above 50 mg/L the accuracy decreases and the suspensions lose stability.

7.3.4 Check reliability of calibration curve by running a standard with every three or four samples.

7.4 Correction for sample color and turbidity:

7.4.1 Run a sample blank using steps 7.1 and 7.2, without the addition of barium chloride (Paragraph 7.1.4).

7.5 Calculation:

7.5.1 Read mg SO_4^{-2} from linear calibration curve:

$$\text{mg } SO_4^{-2}/L = \frac{\text{mg } SO_4^{-2} \times 1{,}000}{\text{mL sample}}$$

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A spike duplicate sample is a sample brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

9.1 Thirty-four analysts in 16 laboratories analyzed six synthetic water samples containing exact increments of inorganic sulfate with the following results:

Increment as Sulfate (mg/L)	Precision as Standard Deviation (mg/L)	Accuracy as Bias (%)	Accuracy as Bias (mg/L)
8.6	2.30	-3.72	-0.3
9.2	1.78	-8.26	-0.8
110	7.86	-3.01	-3.3
122	7.50	-3.37	-4.1
188	9.58	+0.04	+0.1
199	11.8	-1.70	-3.4

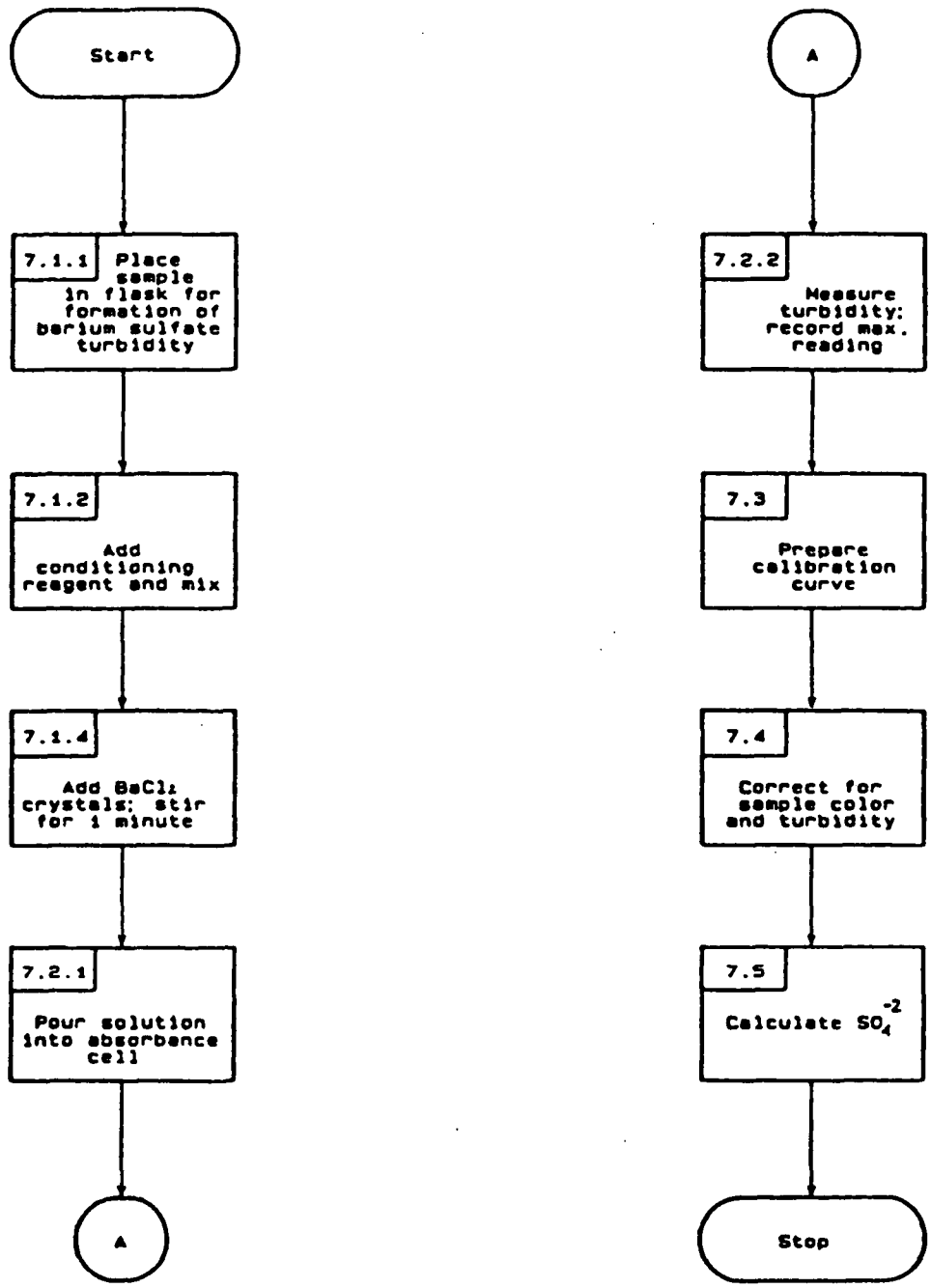
(Data from: FWPCA Method Study 1, Mineral and Physical Analyses.)

9.2 A synthetic unknown sample containing 259 mg/L sulfate, 108 mg/L Ca, 82 mg/L Mg, 3.1 mg/L K, 19.9 mg/L Na, 241 mg/L chloride, 0.250 mg/L nitrite N, 1.1 mg/L nitrate N, and 42.5 mg/L total alkalinity (contributed by $NaHCO_3$), was analyzed in 19 laboratories by the turbidimetric method, with a relative standard deviation of 9.1% and a relative error of 1.2%.

10.0 REFERENCES

1. Annual Book of ASTM Standards, Part 31, "Water," Standard D516-68, Method B, p. 430 (1976).

2. Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 496, Method 427C, (1975).


Start
7.1.1 Place sample in flask for formation of barium sulfate turbidity
7.1.2 Add conditioning reagent and mix
7.1.4 Add BaCl2 crystals; stir for 1 minute
7.2.1 Pour solution into absorbance cell
A
A
7.2.2 Measure turbidity: record max. reading
7.3 Prepare calibration curve
7.4 Correct for sample color and turbidity
7.5 Calculate SO_4^{-2}
Stop

METHOD 9056

DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 This method addresses the sequential determination of the anions chloride, fluoride, bromide, nitrate, nitrite, phosphate, and sulfate in the collection solutions from the bomb combustion of solid waste samples, as well as all water samples.

1.2 The method detection limit (MDL), the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero, varies for anions as a function of sample size and the conductivity scale used. Generally, minimum detectable concentrations are in the range of 0.05 mg/L for F^- and 0.1 mg/L for Br^-, Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^{2-} with a 100-μL sample loop and a 10-μmho full-scale setting on the conductivity detector. Similar values may be achieved by using a higher scale setting and an electronic integrator. Idealized detection limits of an order of magnitude lower have been determined in reagent water by using a 1-μmho/cm full-scale setting (Table 1). The upper limit of the method is dependent on total anion concentration and may be determined experimentally. These limits may be extended by appropriate dilution.

2.0 SUMMARY OF METHOD

2.1 A small volume of combustate collection solution or other water sample, typically 2 to 3 mL, is injected into an ion chromatograph to flush and fill a constant volume sample loop. The sample is then injected into a stream of carbonate-bicarbonate eluent of the same strength as the collection solution or water sample.

2.2 The sample is pumped through three different ion exchange columns and into a conductivity detector. The first two columns, a precolumn or guard column and a separator column, are packed with low-capacity, strongly basic anion exchanger. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The last column is a suppressor column that reduces the background conductivity of the eluent to a low or negligible level and converts the anions in the sample to their corresponding acids. The separated anions in their acid form are measured using an electrical-conductivity cell. Anions are identified based on their retention times compared to known standards. Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve generated from known standards.

3.0 INTERFERENCES

3.1 Any species with a retention time similar to that of the desired ion will interfere. Large quantities of ions eluting close to the ion of interest will also result in an interference. Separation can be improved by adjusting the eluent concentration and/or flow rate. Sample dilution and/or the use of the method of standard additions can also be used. For example, high levels of organic acids may be present in industrial wastes, which may interfere with

inorganic anion analysis. Two common species, formate and acetate, elute between fluoride and chloride.

3.2 Because bromide and nitrate elute very close together, they are potential interferences for each other. It is advisable not to have Br^-/NO_3^- ratios higher than 1:10 or 10:1 if both anions are to be quantified. If nitrate is observed to be an interference with bromide, use of an alternate detector (e.g., electrochemical detector) is recommended.

3.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

3.4 Samples that contain particles larger than 0.45 μm and reagent solutions that contain particles larger than 0.20 μm require filtration to prevent damage to instrument columns and flow systems.

3.5 If a packed bed suppressor column is used, it will be slowly consumed during analysis and, therefore, will need to be regenerated. Use of either an anion fiber suppressor or an anion micromembrane suppressor eliminates the time-consuming regeneration step through the use of a continuous flow of regenerant.

4.0 APPARATUS AND MATERIALS

4.1 Ion chromatograph, capable of delivering 2 to 5 mL of eluent per minute at a pressure of 200 to 700 psi (1.3 to 4.8 MPa). The chromatograph shall be equipped with an injection valve, a 100-μL sample loop, and set up with the following components, as schematically illustrated in Figure 1.

4.1.1 Precolumn, a guard column placed before the separator column to protect the separator column from being fouled by particulates or certain organic constituents (4 x 50 mm, Dionex P/N 030825 [normal run], or P/N 030830 [fast run], or equivalent).

4.1.2 Separator column, a column packed with low-capacity pellicular anion exchange resin that is styrene divinylbenzene-based has been found to be suitable for resolving F^-, Cl^-, NO_2^-, PO_4^{-3}, Br^-, NO_3^-, and SO_4^{-2} (see Figure 2) (4 x 250 mm, Dionex P/N 03827 [normal run], or P/N 030831 [fast run], or equivalent).

4.1.3 Suppressor column, a column that is capable of converting the eluent and separated anions to their respective acid forms (fiber, Dionex P/N 35350, micromembrane, Dionex P/N 38019 or equivalent).

4.1.4 Detector, a low-volume, flowthrough, temperature-compensated, electrical conductivity cell (approximately 6 μL volume, Dionex, or equivalent) equipped with a meter capable of reading from 0 to 1,000 μseconds/cm on a linear scale.

4.1.5 Pump, capable of delivering a constant flow of approximately 2 to 5 mL/min throughout the test and tolerating a pressure of 200 to 700 psi (1.3 to 4.8 MPa).

4.2 Recorder, compatible with the detector output with a full-scale response time in 2 seconds or less.

4.3 Syringe, minimum capacity of 2 mL and equipped with a male pressure fitting.

4.4 Eluent and regenerant reservoirs, suitable containers for storing eluents and regenerant. For example, 4 L collapsible bags can be used.

4.5 Integrator, to integrate the area under the chromatogram. Different integrators can perform this task when compatible with the electronics of the detector meter or recorder. If an integrator is used, the maximum area measurement must be within the linear range of the integrator.

4.6 Analytical balance, capable of weighing to the nearest 0.0001 g.

4.7 Pipets, Class A volumetric flasks, beakers: assorted sizes.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One. Column life may be extended by passing reagent water through a 0.22-μm filter prior to use.

5.3 Eluent, 0.003M $NaHCO_3$/0.0024M Na_2CO_3. Dissolve 1.0080 g of sodium bicarbonate (0.003M $NaHCO_3$) and 1.0176 g of sodium carbonate (0.0024M Na_2CO_3) in reagent water and dilute to 4 L with reagent water.

5.4 Suppressor regenerant solution. Add 100 mL of 1N H_2SO_4 to 3 L of reagent water in a collapsible bag and dilute to 4 L with reagent water.

5.5 Stock solutions (1,000 mg/L).

5.5.1 Bromide stock solution (1.00 mL = 1.00 mg Br^-). Dry approximately 2 g of sodium bromide (NaBr) for 6 hours at 150°C, and cool in a desiccator. Dissolve 1.2877 g of the dried salt in reagent water, and dilute to 1 L with reagent water.

5.5.2 Chloride stock solution (1.00 mL = 1.00 mg Cl^-). Dry sodium chloride (NaCl) for 1 hour at 600°C, and cool in a desiccator. Dissolve 1.6484 g of the dry salt in reagent water, and dilute to 1 L with reagent water.

5.5.3 Fluoride stock solution (1.00 mL = 1.00 mg F^-). Dissolve 2.2100 g of sodium fluoride (NaF) in reagent water, and dilute to 1 L with reagent water. Store in chemical-resistant glass or polyethylene.

5.5.4 Nitrate stock solution (1.00 mL = 1.00 mg NO_3^-). Dry approximately 2 g of sodium nitrate ($NaNO_3$) at 105°C for 24 hours. Dissolve exactly 1.3707 g of the dried salt in reagent water, and dilute to 1 L with reagent water.

5.5.5 Nitrite stock solution (1.00 mL = 1.00 mg NO_2^-). Place approximately 2 g of sodium nitrate ($NaNO_2$) in a 125 mL beaker and dry to constant weight (about 24 hours) in a desiccator containing concentrated H_2SO_4. Dissolve 1.4998 g of the dried salt in reagent water, and dilute to 1 L with reagent water. Store in a sterilized glass bottle. Refrigerate and prepare monthly.

NOTE: Nitrite is easily oxidized, especially in the presence of moisture, and only fresh reagents are to be used.

NOTE: Prepare sterile bottles for storing nitrite solutions by heating for 1 hour at 170°C in an air oven.

5.5.6 Phosphate stock solution (1.00 mL = 1.00 mg PO_4^{3-}). Dissolve 1.4330 g of potassium dihydrogen phosphate (KH_2PO_4) in reagent water, and dilute to 1 L with reagent water. Dry sodium sulfate (Na_2SO_4) for 1 hour at 105°C and cool in a desiccator.

5.5.7 Sulfate stock solution (1.00 mL = 1.00 mg SO_4^{2-}). Dissolve 1.4790 g of the dried salt in reagent water, and dilute to 1 L with reagent water.

5.6 Anion working solutions. Prepare a blank and at least three different working solutions containing the following combinations of anions. The combination anion solutions must be prepared in Class A volumetric flasks. See Table 2.

5.6.1 Prepare a high-range standard solution by diluting the volumes of each anion specified in Table 2 together to 1 L with reagent water.

5.6.2 Prepare the intermediate-range standard solution by diluting 10.0 mL of the high-range standard solution (see Table 2) to 100 mL with reagent water.

5.6.3 Prepare the low-range standard solution by diluting 20.0 mL of the intermediate-range standard solution (see Table 2) to 100 mL with reagent water.

5.7 Stability of standards. Stock standards are stable for at least 1 month when stored at 4°C. Dilute working standards should be prepared weekly, except those that contain nitrite and phosphate, which should be prepared fresh daily.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Analyze the samples as soon as possible after collection. Preserve by refrigeration at 4°C.

7.0 PROCEDURE

7.1 Calibration

7.1.1 Establish ion chromatographic operating parameters equivalent to those indicated in Table 1.

7.1.2 For each analyte of interest, prepare calibration standards at a minimum of three concentration levels and a blank by adding accurately measured volumes of one or more stock standards to a Class A volumetric flask and diluting to volume with reagent water. If the working range exceeds the linear range of the system, a sufficient number of standards must be analyzed to allow an accurate calibration curve to be established. One of the standards should be representative of a concentration near, but above, the method detection limit if the system is operated on an applicable attenuator range. The other standards should correspond to the range of concentrations expected in the sample or should define the working range of the detector. Unless the attenuator range settings are proven to be linear, each setting must be calibrated individually.

7.1.3 Using injections of 0.1 to 1.0 mL (determined by injection loop volume) of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded.

7.1.4 The working calibration curve must be verified on each working day, or whenever the anion eluent strength is changed, and for every batch of samples. If the response or retention time for any analyte varies from the expected values by more than $\pm$ 10%, the test must be repeated, using fresh calibration standards. If the results are still more than $\pm$ 10%, an entirely new calibration curve must be prepared for that analyte.

7.1.5 Nonlinear response can result when the separator column capacity is exceeded (overloading). Maximum column loading (all anions) should not exceed about 400 ppm.

7.2 Analyses

7.2.1 Sample preparation. When aqueous samples are injected, the water passes rapidly through the columns, and a negative "water dip" is observed that may interfere with the early-eluting fluoride and/or chloride ions. The water dip should not be observed in the combustate samples; the collecting solution is a concentrated eluent solution that will "match" the eluent strength when diluted to 100-mL with reagent water according to the bomb combustion procedure. Any dilutions required in analyzing other water samples should be made with the eluent solution. The water dip, if present, may be removed by adding concentrated eluent to

all samples and standards. When a manual system is used, it is necessary to micropipet concentrated buffer into each sample. The recommended procedures follow:

(1) Prepare a 100-mL stock of eluent 100 times normal concentration by dissolving 2.5202 g $NaHCO_3$ and 2.5438 g Na_2CO_3 in 100-mL reagent water. Protect the volumetric flask from air.

(2) Pipet 5 mL of each sample into a clean polystyrene micro-beaker. Micropipet 50 μL of the concentrated buffer into the beaker and stir well.

Dilute the samples with eluent, if necessary, to concentrations within the linear range of the calibration.

7.2.2 Sample analysis.

7.2.2.1 Start the flow of regenerant through the suppressor column.

7.2.2.2 Set up the recorder range for maximum sensitivity and any additional ranges needed.

7.2.2.3 Begin to pump the eluent through the columns. After a stable baseline is obtained, inject a midrange standard. If the peak height deviates by more than 10% from that of the previous run, prepare fresh standards.

7.2.2.4 Begin to inject standards starting with the highest concentration standard and decreasing in concentration. The first sample should be a quality control reference sample to check the calibration.

7.2.2.5 Using the procedures described in Step 7.2.1, calculate the regression parameters for the initial standard curve. Compare these values with those obtained in the past. If they exceed the control limits, stop the analysis and look for the problem.

7.2.2.6 Inject a quality control reference sample. A spiked sample or a sample of known content must be analyzed with each batch of samples. Calculate the concentration from the calibration curve and compare the known value. If the control limits are exceeded, stop the analysis until the problem is found. Recalibration is necessary.

7.2.2.7 When an acceptable value has been obtained for the quality control sample, begin to inject the samples.

7.2.2.8 Load and inject a fixed amount of well-mixed sample. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the

resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

7.2.2.9 The width of the retention time window used to make identifications should be based on measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

7.2.2.10 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

7.2.2.11 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, spike the sample with an appropriate amount of standard and reanalyze.

NOTE: Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases, this peak migration can produce poor resolution or misidentification.

7.3 Calculation

7.3.1 Prepare separate calibration curves for each anion of interest by plotting peak size in area, or peak height units of standards against concentration values. Compute sample concentration by comparing sample peak response with the standard curve.

7.3.2 Enter the calibration standard concentrations and peak heights from the integrator or recorder into a calculator with linear least squares capabilities.

7.3.3 Calculate the following parameters: slope (s), intercept (I), and correlation coefficient (r). The slope and intercept define a relationship between the concentration and instrument response of the form:

$$y_i = s_i\, x_i + I \quad (1)$$

where:

y_i = predicted instrument response
s_i = response slope
x_i = concentration of standard i
I = intercept

Rearrangement of the above equation yields the concentration corresponding to an instrumental measurement:

$$x_j = (y_j - I)/s_j \quad (2)$$

where:

x_j = calculated concentration for a sample
y_j = actual instrument response for a sample
s_j and I are calculated slope and intercept from calibration above.

7.3.4 Enter the sample peak height into the calculator, and calculate the sample concentration in milligrams per liter.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference and inspection. Refer to Chapter One for additional quality control guidelines.

8.2 After every 10 injections, analyze a midrange calibration standard. If the instrument response has changed by more than 5%, recalibrate.

8.3 Analyze one in every ten samples in duplicate. Take the duplicate sample through the entire sample preparation and analytical process.

8.4 A matrix spiked sample should be run for each analytical batch or twenty samples, whatever is more frequent, to determine matrix effects.

9.0 METHOD PERFORMANCE

9.1 Single-operator accuracy and precision for reagent, drinking and surface water, and mixed domestic and industrial wastewater are listed in Table 3.

9.2 Combustate samples. These data are based on 41 data points obtained by six laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. The oil samples were combusted using Method 5050. A data point represents one duplicate analysis of a sample. One data point was judged to be an outlier and was not included in the results.

9.2.1 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the sample operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 4):

*where x is the average of two results in μg/g.

$$Repeatability = 20.9\sqrt{x}*$$

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$Reproducibility = 42.1\sqrt{x}*$$

*where x is the average value of two results in $\mu g/g$.

9.2.2 Bias. The bias of this method varies with concentration, as shown in Table 5:

Bias = Amount found - Amount expected

10.0 REFERENCES

1. Environmental Protection Agency. Test Method for the Determination of Inorganic Anions in Water by Ion Chromatography. EPA Method 300.0. EPA-600/4-84-017. 1984.

2. Annual Book of ASTM Standards, Volume 11.01 Water D4327, Standard Test Method for Anions in Water by Ion Chromatography, pp. 696-703. 1988.

3. Standard Methods for the Examination of Water and Wastewater, Method 429, "Determination of Anions by Ion Chromatography with Conductivity Measurement," 16th Edition of Standard Methods.

4. Dionex, IC 16 Operation and Maintenance Manual, PN 30579, Dionex Corp., Sunnyvale, CA 94086.

5. Method detection limit (MDL) as described in "Trace Analyses for Wastewater," J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, Environmental Science and Technology, Vol. 15, Number 12, p. 1426, December 1981.

6. Gaskill, A.; Estes, E. D.; Hardison, D. L.; and Myers, L. E. Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels. Prepared for U.S. Environmental Protection Agency Office of Solid Waste. EPA Contract No. 68-01-7075, WA 80. July 1988.

TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS IN REAGENT WATER

Analyte	Retention[a] time min	Relative retention time	Method[b] detection limit, mg/L
Fluoride	1.2	1.0	0.005
Chlorine	3.4	2.8	0.015
Nitrite-N	4.5	3.8	0.004
o-Phosphate-P	9.0	7.5	0.061
Nitrate-N	11.3	9.4	0.013
Sulfate	21.4	17.8	0.206

Standard conditions:

Columns - As specified in 4.1.1-4.1.3
Detector - As specified in 4.1.4
Eluent - As specified in 5.3
Sample loop - 100 µL
Pump volume - 2.30 mL/min

Concentrations of mixed standard (mg/L):

Fluoride 3.0
Chloride 4.0
Nitrite-N 10.0
o-Phosphate-P 9.0
Nitrate-N 30.0
Sulfate 50.0

[a]The retention time given for each anion is based on the equipment and analytical conditions described in the method. Use of other analytical columns or different elutant concentrations will effect retention times accordingly.

[b]MDL calculated from data obtained using an attentuator setting of 1-µmho/cm full scale. Other settings would produce an MDL proportional to their value.

TABLE 2.
PREPARATION OF STANDARD SOLUTIONS FOR INSTRUMENT CALIBRATION

	High Range Standard[1]	Anion concentration mg/L	Intermediate-range standard, mg/L (see 5.6.2)	Low-range standard, mg/L (see 5.6.3)
Fluoride (F^-)	10	10	1.0	0.2
Chloride (Cl^-)	10	10	1.0	0.2
Nitrite (NO_2^-)	20	20	2.0	0.4
Phosphate (PO_4^{3-})	50	50	5.0	1.0
Bromide (Br^-)	10	10	1.0	0.2
Nitrate (NO_3^-)	30	30	3.0	0.6
Sulfate (SO_4^{2-})	100	100	10.0	2.0

[1]Milliliters of each stock solution (1.00 mL = 1.00 mg) diluted to 1 L (see sec. 5.6.1).

TABLE 3.
SINGLE-OPERATOR ACCURACY AND PRECISION

Analyte	Sample type	Spike mg/L	Number of replicates	Mean recovery, %	Standard deviation, mg/L
Chloride	RW	0.050	7	97.7	0.0047
	DW	10.0	7	98.2	0.289
	SW	1.0	7	105.0	0.139
	WW	7.5	7	82.7	0.445
Fluoride	RW	0.24	7	103.1	0.0009
	DW	9.3	7	87.7	0.075
	SW	0.50	7	74.0	0.0038
	WW	1.0	7	92.0	0.011
Nitrate-N	RW	0.10	7	100.9	0.0041
	DW	31.0	7	100.7	0.356
	SW	0.50	7	100.0	0.0058
	WW	4.0	7	94.3	0.058
Nitrite-N	RW	0.10	7	97.7	0.0014
	DW	19.6	7	103.3	0.150
	SW	0.51	7	88.2	0.0053
	WW	0.52	7	100.0	0.018
o-Phosphate-P	RW	0.50	7	100.4	0.019
	DE	45.7	7	102.5	0.386
	SW	0.51	7	94.1	0.020
	WW	4.0	7	97.3	0.04
Sulfate	RW	1.02	7	102.1	0.066
	DW	98.5	7	104.3	1.475
	SW	10.0	7	111.6	0.709
	WW	12.5	7	134.9	0.466

RW = Reagent water. SW = Surface water.
DW = Drinking water. WW = Wastewater.

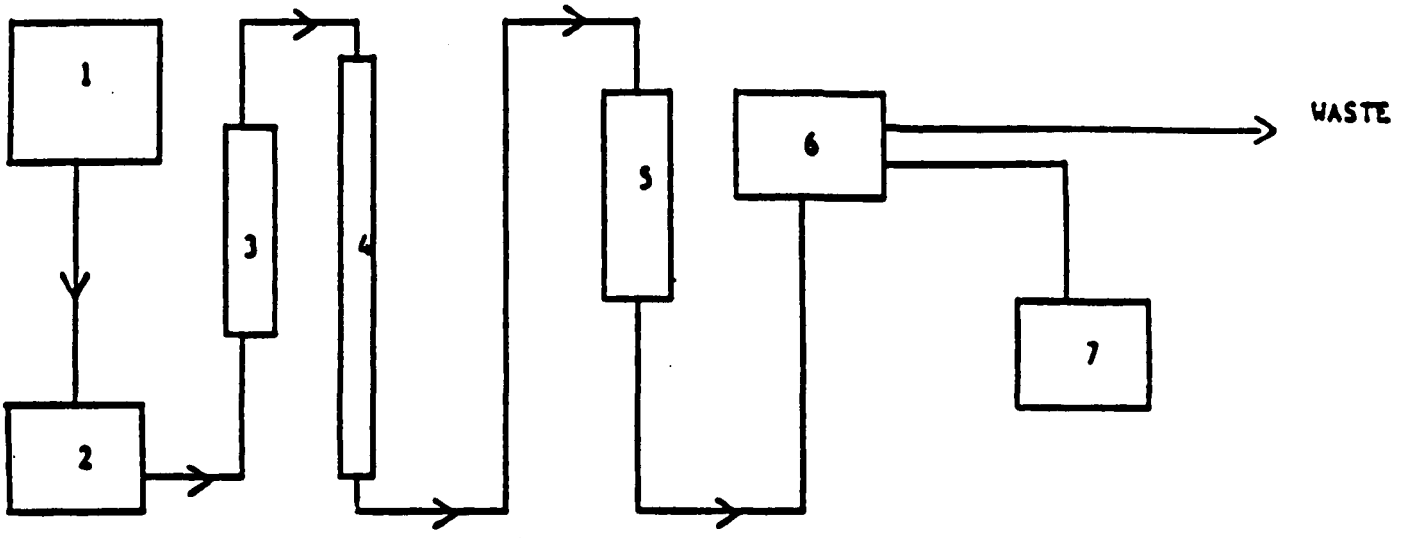
TABLE 4.
REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND ION CHROMATOGRAPHY

Average value, µg/g	Repeatability, µg/g	Reproducibility, µg/g
500	467	941
1,000	661	1,331
1,500	809	1,631
2,000	935	1,883
2,500	1,045	2,105
3,000	1,145	2,306

TABLE 5.
RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND ION CHROMATOGRAPHY

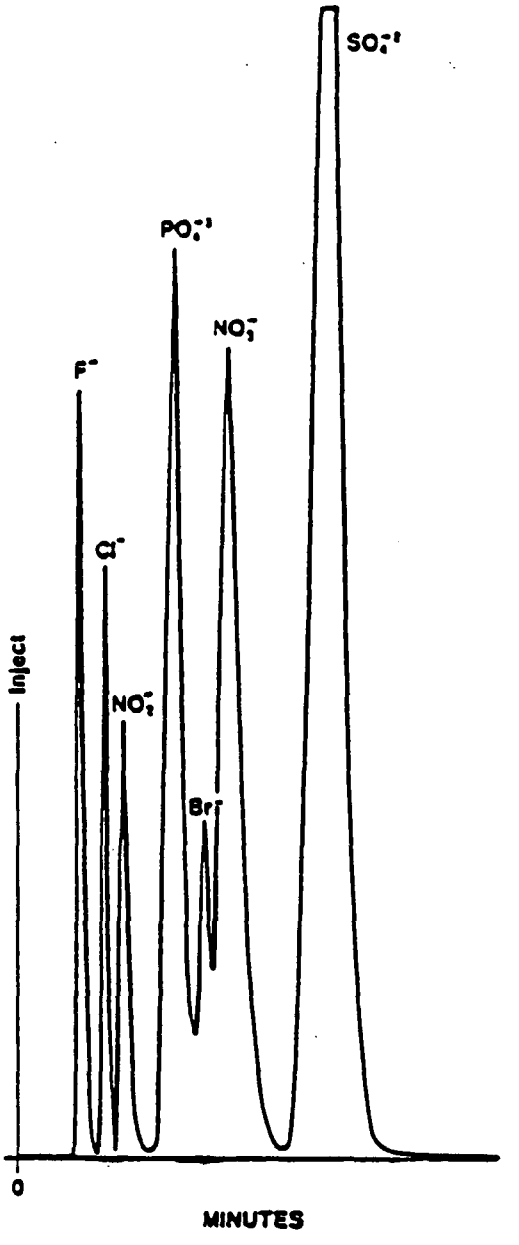
Amount Expected µg/g	Amount found µg/g	Bias, µg/g	Percent, bias
320	567	247	+77
480	773	293	+61
920	1,050	130	+14
1,498	1,694	196	+13
1,527	1,772	245	+16
3,029	3,026	-3	0
3,045	2,745	-300	-10

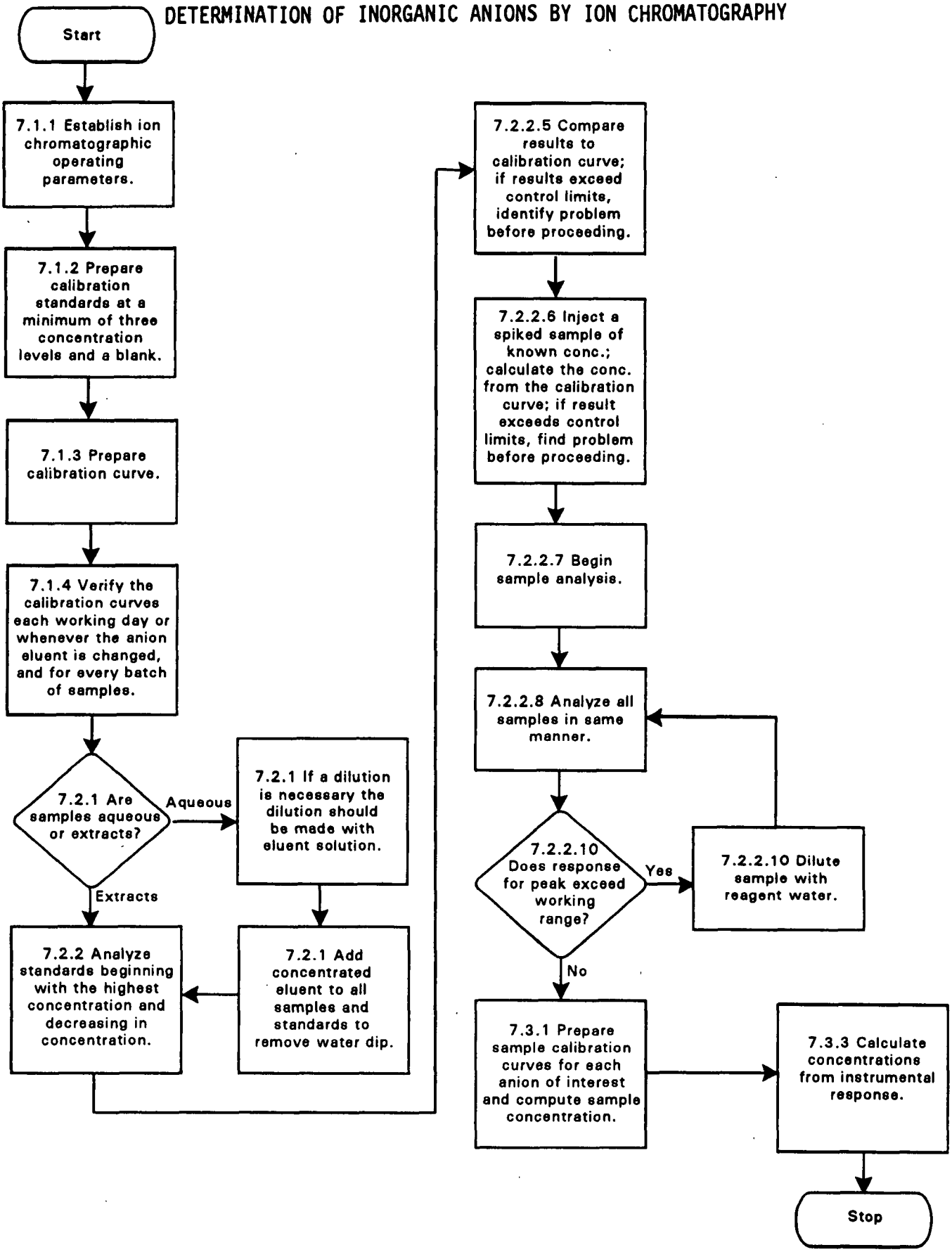
FIGURE 1
SCHEMATIC OF ION CHROMATOGRAPH



(1) Eluent reservoir
(2) Pump
(3) Precolumn
(4) Separator column
(5) Suppressor column
(6) Detector
(7) Recorder or integrator, or both

FIGURE 2
TYPICAL ANION PROFILE




Start
7.1.1 Establish ion chromatographic operating parameters.
7.1.2 Prepare calibration standards at a minimum of three concentration levels and a blank.
7.1.3 Prepare calibration curve.
7.1.4 Verify the calibration curves each working day or whenever the anion eluent is changed, and for every batch of samples.
7.2.1 Are samples aqueous or extracts?
Aqueous
7.2.1 If a dilution is necessary the dilution should be made with eluent solution.
Extracts
7.2.2 Analyze standards beginning with the highest concentration and decreasing in concentration.
7.2.1 Add concentrated eluent to all samples and standards to remove water dip.
7.2.2.5 Compare results to calibration curve; if results exceed control limits, identify problem before proceeding.
7.2.2.6 Inject a spiked sample of known conc.; calculate the conc. from the calibration curve; if result exceeds control limits, find problem before proceeding.
7.2.2.7 Begin sample analysis.
7.2.2.8 Analyze all samples in same manner.
7.2.2.10 Does response for peak exceed working range?
Yes
7.2.2.10 Dilute sample with reagent water.
No
7.3.1 Prepare sample calibration curves for each anion of interest and compute sample concentration.
7.3.3 Calculate concentrations from instrumental response.
Stop

METHOD 9060

TOTAL ORGANIC CARBON

1.0 SCOPE AND APPLICATION

1.1 Method 9060 is used to determine the concentration of organic carbon in ground water, surface and saline waters, and domestic and industrial wastes. Some restrictions are noted in Sections 2.0 and 3.0.

1.2 Method 9060 is most applicable to measurement of organic carbon above 1 mg/L.

2.0 SUMMARY OF METHOD

2.1 Organic carbon is measured using a carbonaceous analyzer. This instrument converts the organic carbon in a sample to carbon dioxide (CO_2) by either catalytic combustion or wet chemical oxidation. The CO_2 formed is then either measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 in a sample is directly proportional to the concentration of carbonaceous material in the sample.

2.2 Carbonaceous analyzers are capable of measuring all forms of carbon in a sample. However, because of various properties of carbon-containing compounds in liquid samples, the manner of preliminary sample treatment as well as the instrument settings will determine which forms of carbon are actually measured. The forms of carbon that can be measured by Method 9060 are:

1. Soluble, nonvolatile organic carbon: e.g., natural sugars.
2. Soluble, volatile organic carbon: e.g., mercaptans, alkanes, low molecular weight alcohols.
3. Insoluble, partially volatile carbon: e.g., low molecular weight oils.
4. Insoluble, particulate carbonaceous materials: e.g., cellulose fibers.
5. Soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter: e.g., oily matter adsorbed on silt particles.

2.3 Carbonate and bicarbonate are inorganic forms of carbon and must be separated from the total organic carbon value. Depending on the instrument manufacturer's instructions, this separation can be accomplished by either a simple mathematical subtraction, or by removing the carbonate and bicarbonate by converting them to CO_2 with degassing prior to analysis.

3.0 INTERFERENCES

3.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

3.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter-type syringe or pipet. The openings of the syringe or pipet limit the maximum size of particle which may be included in the sample.

3.3 Removal of carbonate and bicarbonate by acidification and purging with nitrogen, or other inert gas, can result in the loss of volatile organic substances.

4.0 APPARATUS AND MATERIALS

4.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

4.2 Apparatus for total and dissolved organic carbon:

4.2.1 Several companies manufacture analyzers for measuring carbonaceous material in liquid samples. The most appropriate system should be selected based on consideration of the types of samples to be analyzed, the expected concentration range, and the forms of carbon to be measured.

4.2.2 No specific analyzer is recommended as superior. If the technique of chemical oxidation is used, the laboratory must be certain that the instrument is capable of achieving good carbon recoveries in samples containing particulates.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities, and should be boiled and cooled to remove CO_2.

5.2 Potassium hydrogen phthalate, stock solution, 1,000 mg/L carbon: Dissolve 0.2128 g of potassium hydrogen phthalate (primary standard grade) in Type II water and dilute to 100.0 mL.

NOTE: Sodium oxalate and acetic acid are not recommended as stock solutions.

5.3 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with Type II water.

5.4 Carbonate-bicarbonate, stock solution, 1,000 mg/L carbon: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100-mL volumetric flask. Dissolve with Type II water.

5.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to Step 5.3.

NOTE: This standard is not required by some instruments.

5.6 Blank solution: Use the same Type II water as was used to prepare the standard solutions.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples.

NOTE: A brief study performed in the EPA Laboratory indicated that Type II water stored in new, 1-qt cubitainers did not show any increase in organic carbon after 2 weeks' exposure.

6.3 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the time between sample collection and the start of analysis should be minimized. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

6.4 In instances where analysis cannot be performed within 2 hr from time of sampling, the sample is acidified ($pH \leq 2$) with HCl or H_2SO_4.

7.0 PROCEDURE

7.1 Homogenize the sample in a blender.

NOTE: To avoid erroneously high results, inorganic carbon must be accounted for. The preferred method is to measure total carbon and inorganic carbon and to obtain the organic carbon by subtraction. If this is not possible, follow Steps 7.2 and 7.3 prior to analysis; however, volatile organic carbon may be lost.

7.2 Lower the pH of the sample to 2.

7.3 Purge the sample with nitrogen for 10 min.

7.4 Follow instrument manufacturer's instructions for calibration, procedure, and calculations.

7.5 For calibration of the instrument, a series of standards should be used that encompasses the expected concentration range of the samples.

7.6 Quadruplicate analysis is required. Report both the average and the range.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 Verify calibration with an independently prepared check standard every 15 samples.

8.4 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

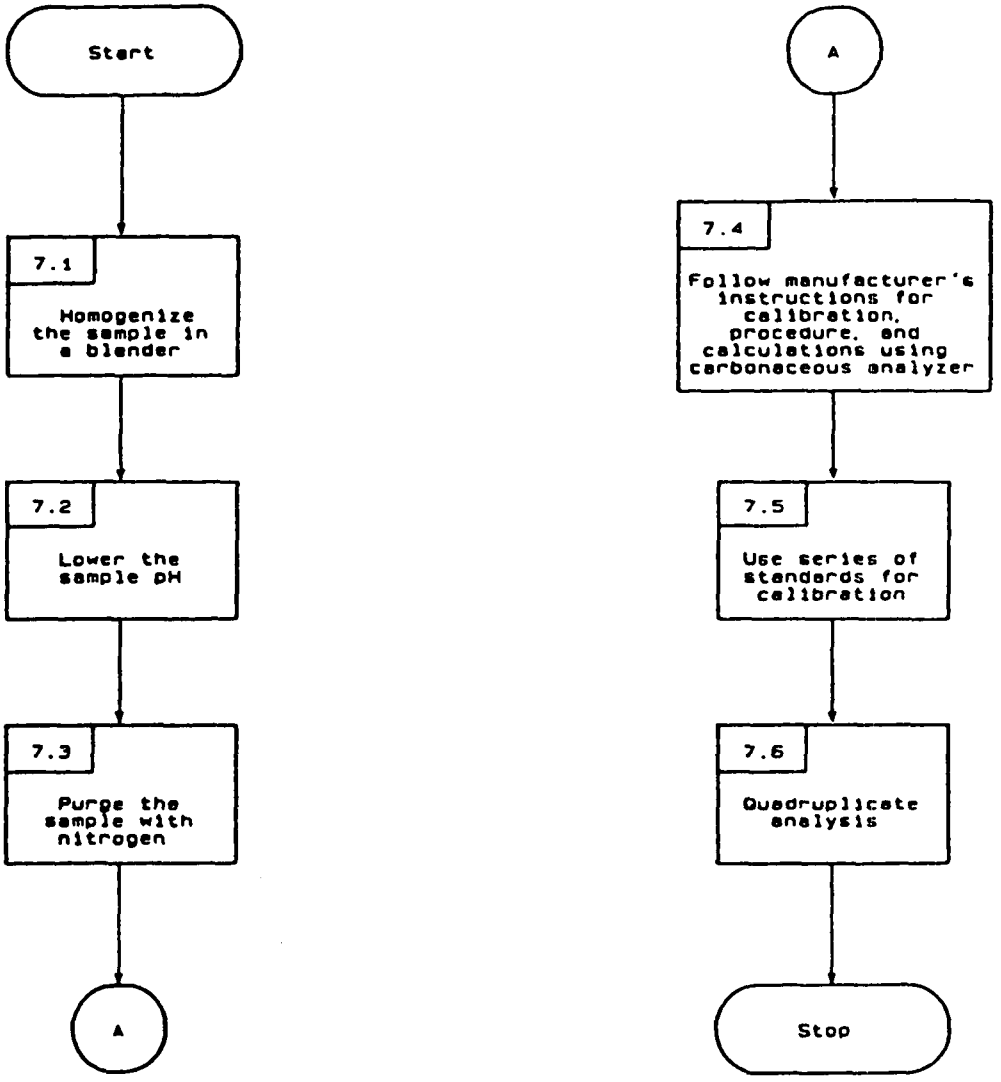
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 415.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Annual Book of ASTM Standards, Part 31, "Water," Standard D 2574-79, p. 469 (1976).

2. Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 532, Method 505 (1975).


Start
7.1
Homogenize the sample in a blender
7.2
Lower the sample pH
7.3
Purge the sample with nitrogen
A
A
7.4
Follow manufacturer's instructions for calibration, procedure, and calculations using carbonaceous analyzer
7.5
Use series of standards for calibration
7.6
Quadruplicate analysis
Stop

METHOD 9065

PHENOLICS (SPECTROPHOTOMETRIC, MANUAL 4-AAP WITH DISTILLATION)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the analysis of ground water, drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 The method is capable of measuring phenolic materials at the 5 ug/L level when the colored end product is extracted and concentrated in a solvent phase using phenol as a standard.

1.3 The method is capable of measuring phenolic materials that contain more than 50 ug/L in the aqueous phase (without solvent extraction) using phenol as a standard.

1.4 It is not possible to use this method to differentiate between different kinds of phenols.

2.0 SUMMARY OF METHOD

2.1 Phenolic materials react with 4-aminoantipyrine in the presence of potassium ferricyanide at a pH of 10 to form a stable reddish-brown antipyrine dye. The amount of color produced is a function of the concentration of phenolic material.

3.0 INTERFERENCES

3.1 For most samples a preliminary distillation is required to remove interfering materials.

3.2 Color response of phenolic materials with 4-aminoantipyrine is not the same for all compounds. Because phenolic-type wastes usually contain a variety of phenols, it is not possible to duplicate a mixture of phenols to be used as a standard. For this reason phenol has been selected as a standard and any color produced by the reaction of other phenolic compounds is reported as phenol. This value will represent the minimum concentration of phenolic compounds present in the sample.

3.3 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of <4 with H_2SO_4 and aerating briefly by stirring.

3.4 Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium sulfate. If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be low.

4.0 APPARATUS AND MATERIALS

4.1 Distillation apparatus: All glass, consisting of a 1-liter Pyrex distilling apparatus with Graham condenser.

4.2 pH meter.

4.3 Spectrophotometer: For use at 460 or 510 nm.

4.4 Funnels.

4.5 Filter paper.

4.6 Membrane filters.

4.7 Separatory funnels: 500- or 1,000-mL.

4.8 Nessler tubes: Short or long form.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Sulfuric acid solution, H_2SO_4: Concentrated.

5.3 Buffer solution: Dissolve 16.9 g NH_4Cl in 143 mL concentrated NH_4OH and dilute to 250 mL with Type II water. Two mL of buffer should adjust 100 mL of distillate to pH 10.

5.4 Aminoantipyrine solution: Dissolve 2 g of 4-aminoantipyrine (4-AAP) in Type II water and dilute to 100 mL.

5.5 Potassium ferricyanide solution: Dissolve 8 g of $K_3Fe(CN)_6$ in Type II water and dilute to 100 mL.

5.6 Stock phenol solution: Dissolve 1.0 g phenol in freshly boiled and cooled Type II water and dilute to 1 liter (1 mL = 1 mg phenol).
NOTE: **This solution is hydroscopic and toxic.**

5.7 Working solution A: Dilute 10 mL stock phenol solution to 1 liter with Type II water (1 mL = 10 ug phenol).

5.8 Working solution B: Dilute 100 mL of working solution A to 1,000 mL with Type II water (1 mL = 1 ug phenol).

5.9 Chloroform.

5.10 Ferrous ammonium sulfate: Dissolve 1.1 g in 500 mL Type II water containing 1 mL concentrated H_2SO_4 and dilute to 1 liter with freshly boiled and cooled Type II water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Biological degradation is inhibited by the addition of H_2SO_4 to pH <4. Store at 4°C. The sample should be stable for 28 days.

7.0 PROCEDURE

7.1 Distillation:

7.1.1 Measure 500 mL of sample into a beaker. Lower the pH to approximately 4 with concentrated H_2SO_4 (1 mL/L), and transfer to the distillation apparatus.

7.1.2 Distill 450 mL of sample, stop the distillation, and when boiling ceases, add 50 mL of warm Type II water to the flask and resume distillation until 500 mL have been collected.

7.1.3 If the distillate is turbid, filter through a prewashed membrane filter.

7.2 Direct photometric method:

7.2.1 Using working solution A (5.6), prepare the following standards in 100-mL volumetric flasks:

Working Solution A (mL)	Concentration (ug/L)
0.0	0.0
0.5	50.0
1.0	100.0
2.0	200.0
5.0	500.0
8.0	800.0
10.0	1000.0

7.2.2 To 100 mL of distillate or to an aliquot diluted to 100 mL and/or standards, add 2 mL of buffer solution (5.2) and mix. The pH of the sample and standards should be 10 $\pm$ 0.2.

7.2.3 Add 2.0 mL aminoantipyrine solution (5.3) and mix.

7.2.4 Add 2.0 mL potassium ferricyanide solution (5.4) and mix.

7.2.5 After 15 min read absorbance at 510 nm.

7.3 Chloroform extraction method:

CAUTION: This method should be performed in a hood; chloroform is toxic.

7.3.1 Using working solution B (5.7), prepare the following standards. Standards may be prepared by pipetting the required volumes into the separatory funnels and diluting to 500 mL with Type II water:

Working Solution B (mL)	Concentration (ug/L)
0.0	0.0
3.0	6.0
5.0	10.0
10.0	20.0
20.0	40.0
25.0	50.0

7.3.2 Place 500 mL of distillate or an aliquot diluted to 500 mL in a separatory funnel. The sample should not contain more than 50 ug/L phenol.

7.3.3 To sample and standards add 10 mL of buffer solution (5.2) and mix. The pH should be 10 $\pm$ 0.2.

7.3.4 Add 3.0 mL aminoantipyrine solution (5.3) and mix.

7.3.5 Add 3.0 mL potassium ferricyanide solution (5.4) and mix.

7.3.6 After 3 min, extract with 25 mL of chloroform (5.9). Shake the separatory funnel at least 10 times, let $CHCl_3$ settle, shake again 10 times, and let chloroform settle again.

7.3.7 Filter chloroform extract through filter paper. Do not add more chloroform.

7.3.8 Read the absorbance of the samples and standards against the blank at 460 nm.

7.4 Calculation:

7.4.1 Prepare a standard curve by plotting the absorbance values of standards versus the corresponding phenol concentrations.

7.4.2 Obtain concentration value of sample directly from standard curve.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

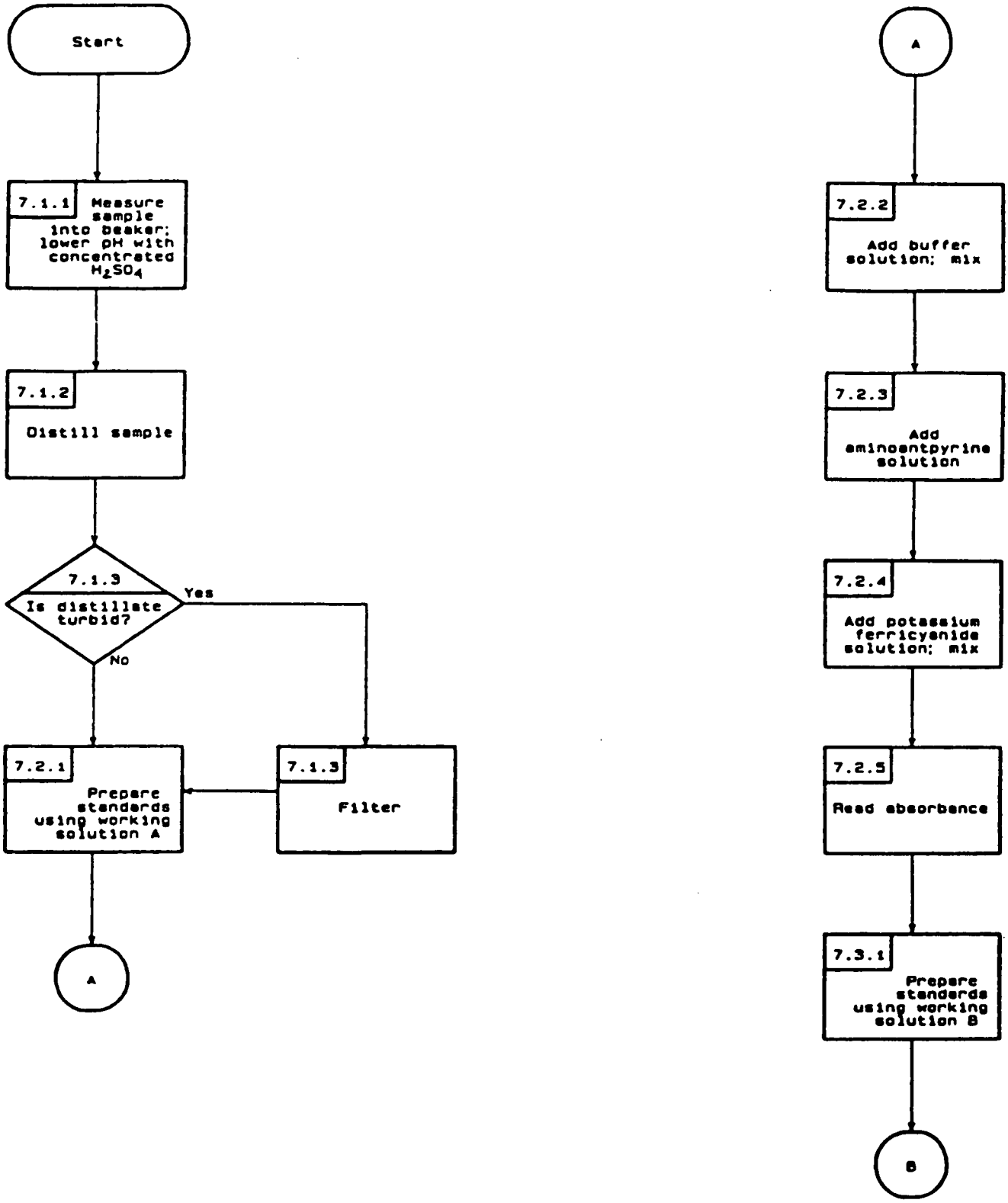
9.1 In a single laboratory using sewage samples at concentrations of 3.8, 15, 43, and and 89 ug/L, the standard deviations were ±0.5, ±0.6, ±0.6, and ±1.0 ug/L, respectively. At concentrations of 73, 146, 299, and 447 ug/L, the standard deviations were ±1.0, ±1.8, ±4.2, and ±5.3 ug/L, respectively.

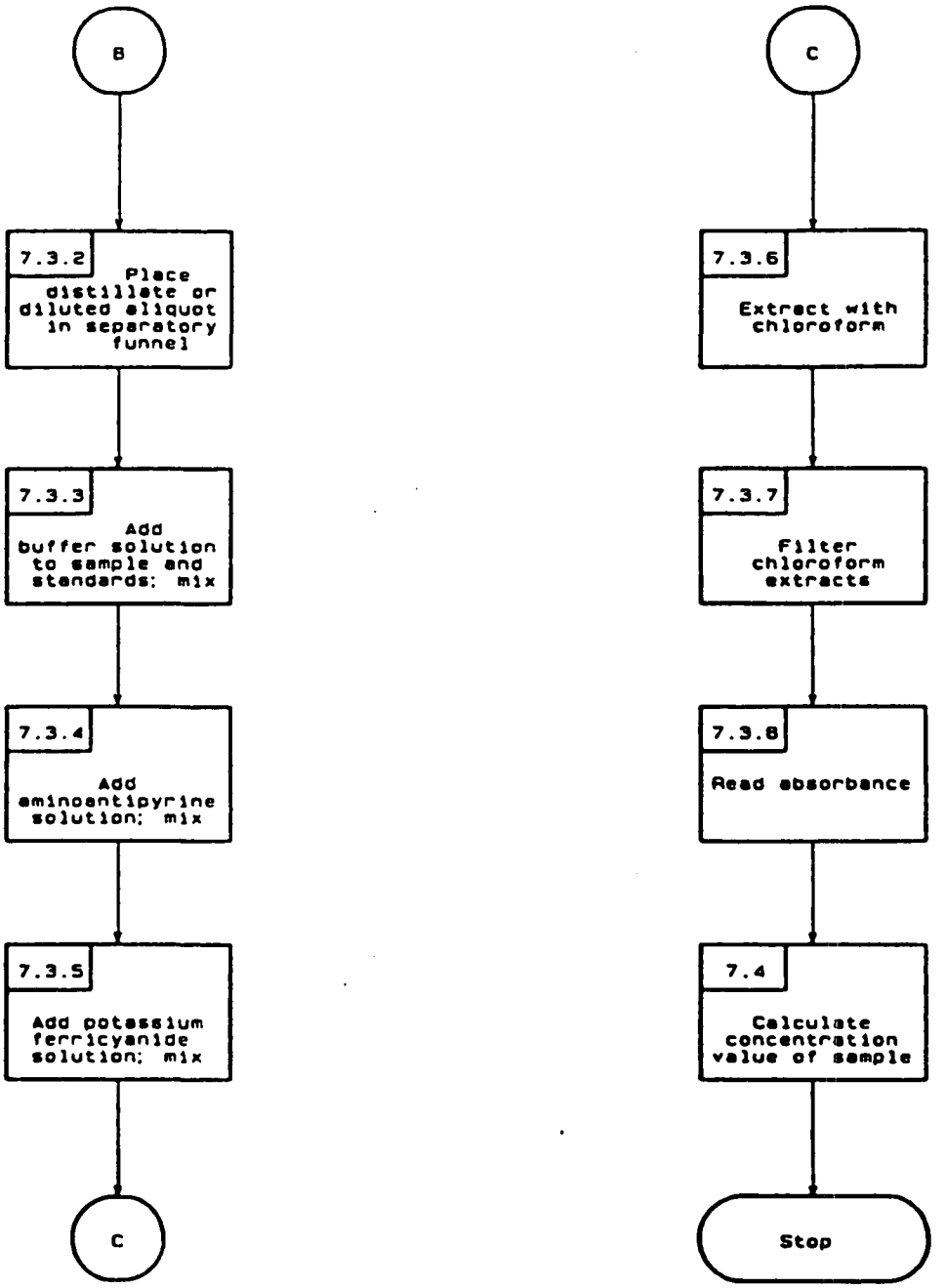
9.2 In a single laboratory using sewage samples at concentrations of 5.3 and 82 ug/L, the recoveries were 78% and 98%,respectively. At concentrations of 168 and 489 ug/L, the recoveries were 97% and 98%, respectively.

10.0 REFERENCES

1. Annual Book of ASTM Standards, Part 31, "Water," Standard D1783-70, p. 553 (1976).

2. Standard Methods for the Examination of Water and Wastewater, 14th ed., pp. 574-581, Method 510 through 510C (1975).


Start
7.1.1 Measure sample into beaker; lower pH with concentrated H_2SO_4
7.1.2 Distill sample
7.1.3 Is distillate turbid?
Yes
No
7.1.3 Filter
7.2.1 Prepare standards using working solution A
A
A
7.2.2 Add buffer solution; mix
7.2.3 Add aminoantpyrine solution
7.2.4 Add potassium ferricyanide solution; mix
7.2.5 Read absorbance
7.3.1 Prepare standards using working solution B
B


B
7.3.2
Place distillate or diluted aliquot in separatory funnel
7.3.3
Add buffer solution to sample and standards; mix
7.3.4
Add aminoantipyrine solution; mix
7.3.5
Add potassium ferricyanide solution; mix
C
C
7.3.6
Extract with chloroform
7.3.7
Filter chloroform extracts
7.3.8
Read absorbance
7.4
Calculate concentration value of sample
Stop

METHOD 9066

PHENOLICS (COLORIMETRIC, AUTOMATED 4-AAP WITH DISTILLATION)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the analysis of ground water and of drinking, surface, and saline waters.

1.2 The method is capable of measuring phenolic materials from 2 to 500 ug/L in the aqueous phase using phenol as a standard.

2.0 SUMMARY OF METHOD

2.1 This automated method is based on the distillation of phenol and subsequent reaction of the distillate with alkaline ferricyanide ($K_3Fe(CN)_6$) and 4-amino-antipyrine (4-AAP) to form a red complex which is measured at 505 or 520 nm.

3.0 INTERFERENCES

3.1 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of <4.0 with H_2SO_4 and aerating briefly by stirring.

3.2 Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium sulfate (5.5). If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be low.

3.3 Background contamination from plastic tubing and sample containers is eliminated by filling the wash receptacle by siphon (using Kel-F tubing) and using glass tubes for the samples and standards.

4.0 APPARATUS AND MATERIALS

4.1 Automated continuous-flow analytical instrument:

4.1.1 Sampler: Equipped with continuous mixer.

4.1.2 Manifold.

4.1.3 Proportioning pump II or III.

4.1.4 Heating bath with distillation coil.

4.1.5 Distillation head.

4.1.6 **Colorimeter:** Equipped with a 50 mm flowcell and 505 or 520 nm filter.

4.1.7 **Recorder.**

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Distillation reagent: Add 100 mL of concentrated phosphoric acid (85% H_3PO_4) to 800 mL of Type II water, cool and dilute to 1 liter.

5.3 Buffered potassium ferricyanide: Dissolve 2.0 g potassium ferricyanide, 3.1 g boric acid, and 3.75 g potassium chloride in 800 mL of Type II water. Adjust to pH of 10.3 with 1 N sodium hydroxide (5.3) and dilute to 1 liter. Add 0.5 mL of Brij-35 (available from Technicon). (Brij-35 is a wetting agent and is a proprietary Technicon product.) Prepare fresh weekly.

5.4 Sodium hydroxide (1 N): Dissolve 40 g NaOH in 500 mL of Type II water, cool and dilute to 1 liter.

5.5 4-Aminoantipyrine: Dissolve 0.65 g of 4-aminoantipyrine in 800 mL of Type II water and dilute to 1 liter. Prepare fresh each day.

5.6 Ferrous ammonium sulfate: Dissolve 1.1 g ferrous ammonium sulfate in 500 mL Type II water containing 1 mL H_2SO_4 and dilute to 1 liter with freshly boiled and cooled Type II water.

5.7 Stock phenol: Dissolve 1.00 g phenol in 500 mL of Type II water and dilute to 1,000 mL. Add 0.5 mL concentrated H_2SO_4 as preservative (1.0 mL = 1.0 mg phenol).

CAUTION: This solution is toxic.

5.8 Standard phenol solution A: Dilute 10.0 mL of stock phenol solution (5.6) to 1,000 mL (1.0 mL = 0.01 mg phenol).

5.9 Standard phenol solution B: Dilute 100.0 mL of standard phenol solution A (5.8) to 1,000 mL with Type II water (1.0 mL = 0.001 mg phenol).

5.10 Standard phenol solution C: Dilute 100.0 mL of standard phenol solution B (5.9) to 1,000 mL with Type II water (1.0 mL = 0.0001 mg phenol).

5.11 Using standard solution A, B, or C, prepare the following standards in 100-mL volumetric flasks. Each standard should be preserved by adding 2 drops of concentrated H_2SO_4 to 100.0 mL:

Standard Solution (mL)	Concentration (ug/L)
Solution C	
1.0	1.0
2.0	2.0
3.0	3.0
5.0	5.0
Solution B	
1.0	10.0
2.0	20.0
5.0	50.0
10.0	100.0
Solution A	
2.0	200.0
3.0	300.0
5.0	500.0

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Biological degradation is inhibited by the acidification to a pH <4 with H_2SO_4. The sample should be kept at 4°C and analyzed within 28 days of collection.

7.0 PROCEDURE

7.1 Set up the manifold as shown in Figure 1.

7.2 Fill the wash receptacle by siphon. Use Kel-F tubing with a fast flow (1 liter/hr).

7.3 Allow colorimeter and recorder to warm up for 30 min. Run a baseline with all reagents, feeding Type II water through the sample line. Use polyethylene tubing for sample line. When new tubing is used, about 2 hr may be required to obtain a stable baseline. This 2-hr time period may be necessary to remove the residual phenol from the tubing.

7.4 Place appropriate phenol standards in sampler in order of decreasing concentration. Complete loading of sampler tray with unknown samples, using glass tubes. If samples have not been preserved as instructed in Paragraph 6.2, add concentrated H_2SO_4 to 100 mL of sample. Run with sensitivity setting at full scale or 500.

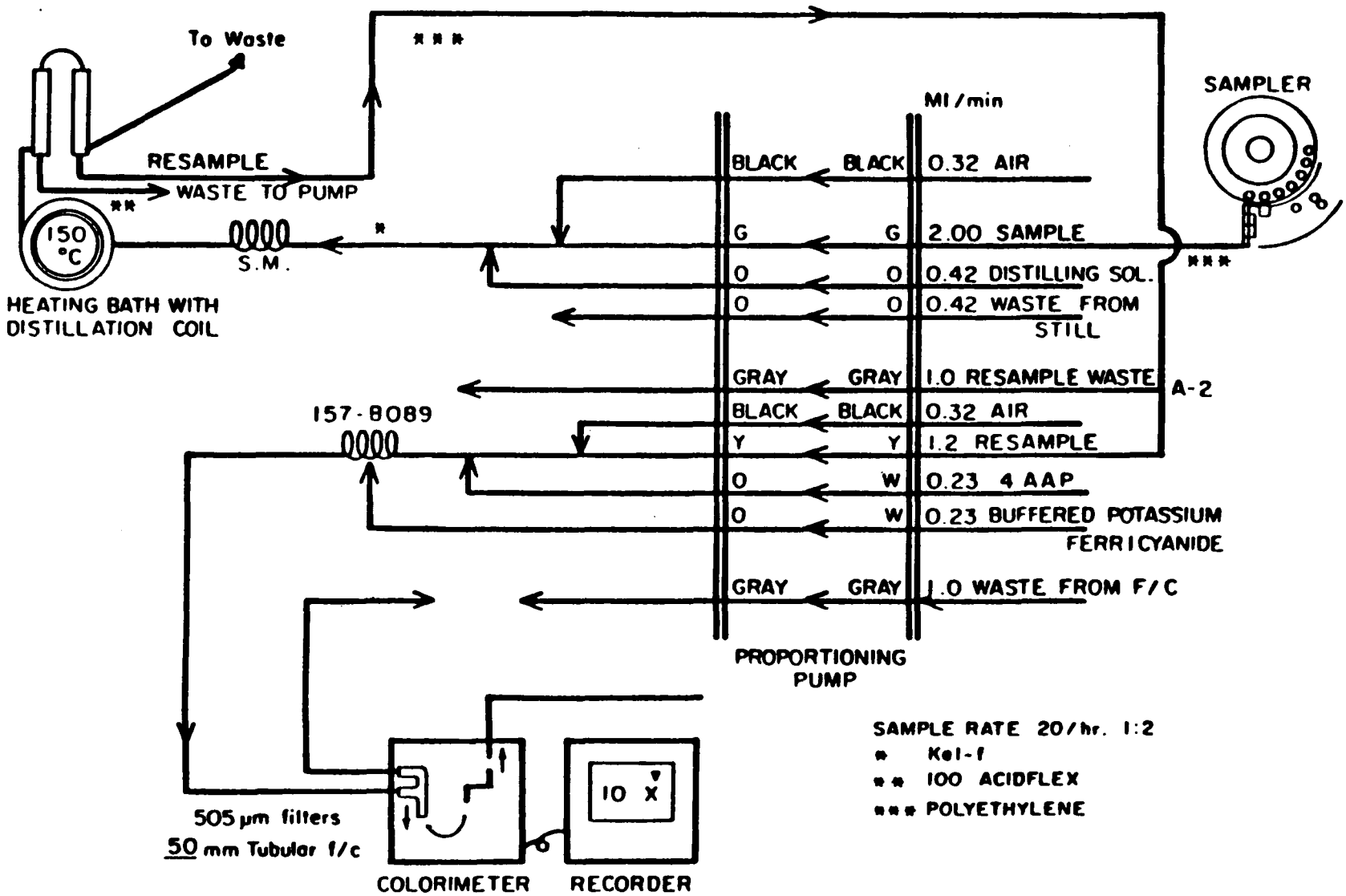


Figure 1. Phenol Autoanalyzer II

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7.5 Switch sample from Type II water to sampler and begin analysis.

7.6 Calculation:

7.6.1 Prepare a linear standard curve by plotting peak heights of standards against concentration values. Compute concentration of samples by comparing sample peak heights with standards.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

9.1 In a single laboratory using sewage samples at concentrations of 3.8, 15, 43, and 89 ug/L, the standard deviations were ±0.5, ±0.6, ±0.6, and ±1.0 ug/L, respectively. At concentrations of 73, 146, 299, and 447 ug/L, the standard deviations were ±1.0, ±1.8, ±4.2, and ±5.3 ug/L, respectively.

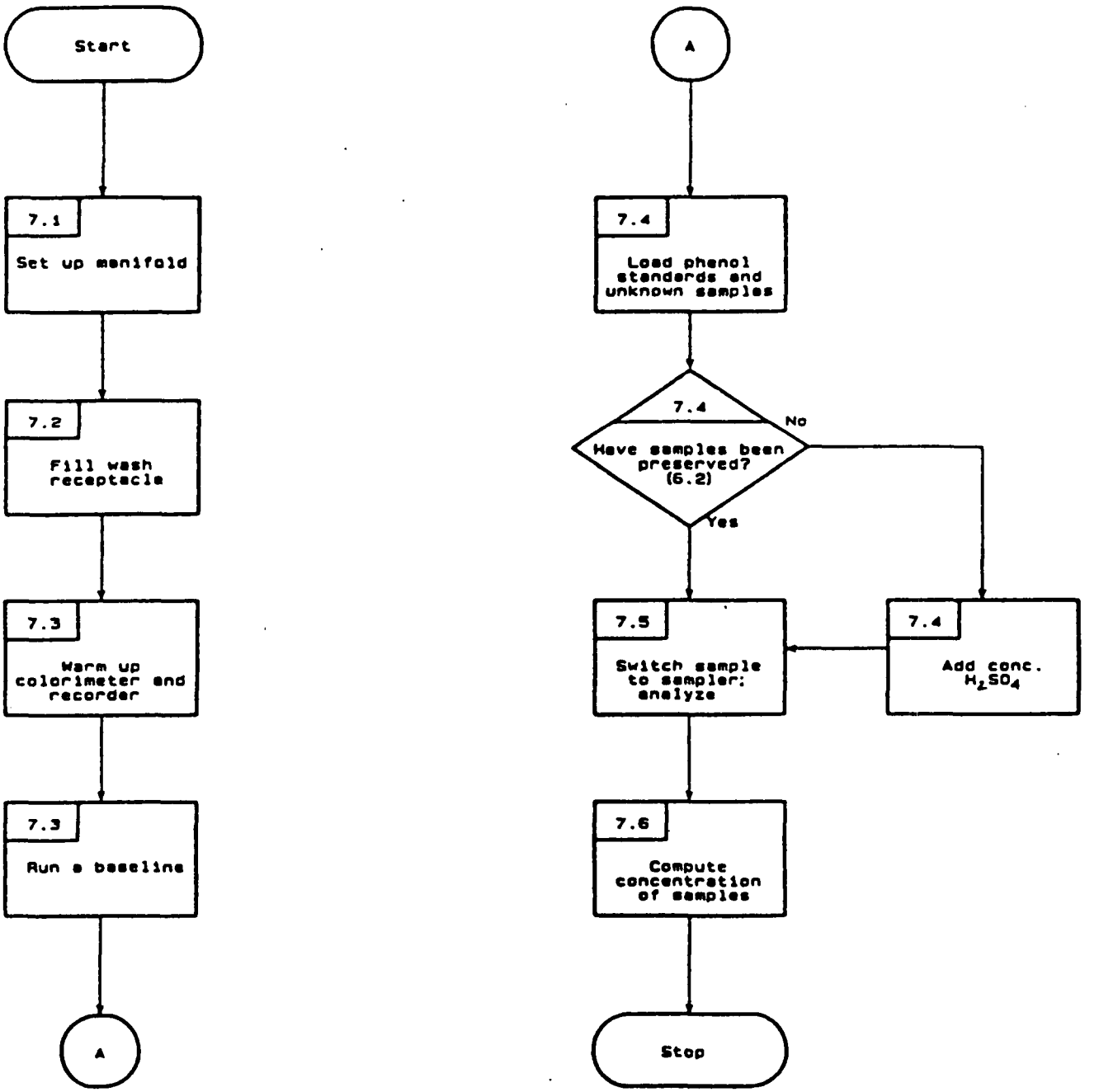
9.2 In a single laboratory using sewage samples at concentrations of 5.3 and 82 ug/L, the recoveries were 78% and 98%, respectively. At concentrations of 168 and 489 ug/L, the recoveries were 97% and 98%, respectively.

10.0 REFERENCES

1. Gales, M.E. and R.L. Booth, "Automated 4AAP Phenolic Method," AWWA 68, 540 (1976).

2. Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 574, Method 510, (1975).

3. Technicon AutoAnalyzer II Methodology, Industrial Method No.127-71W, AA II.


Start
7.1
Set up manifold
7.2
Fill wash receptacle
7.3
Warm up colorimeter and recorder
7.3
Run a baseline
A
A
7.4
Load phenol standards and unknown samples
7.4
Have samples been preserved? (6.2)
No
Yes
7.5
Switch sample to sampler; analyze
7.4
Add conc. H_2SO_4
7.6
Compute concentration of samples
Stop

METHOD 9067

PHENOLICS (SPECTROPHOTOMETRIC, MBTH WITH DISTILLATION)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the analysis of ground water, drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 The method is capable of measuring phenolic materials at the 2 ug/L level when the colored end product is extracted and concentrated in a solvent phase using phenol as a standard.

1.3 The method is capable of measuring phenolic materials that contain from 50 to 1,000 ug/L in the aqueous phase (without solvent extraction) using different kinds of phenols.

1.4 It is not possible to use this method to differentiate between different kinds of phenols.

2.0 SUMMARY OF METHOD

2.1 This method is based on the coupling of phenol with MBTH in an acid medium using ceric ammonium sulfate as an oxidant. The coupling takes place in the p-position; if this position is occupied, the MBTH reagent will react at a free o-position. The colors obtained have maximum absorbance from 460 to 595 nm. For phenol and most phenolic mixtures, the absorbance is 520 and 490 nm.

3.0 INTERFERENCES

3.1 For most samples a preliminary distillation is required to remove interfering materials.

3.2 Color response of phenolic materials with MBTH is not the same for all compounds. Because phenolic-type wastes usually contain a variety of phenols, it is not possible to duplicate a mixture of phenols to be used as a standard. For this reason, phenol has been selected as a standard and any color produced by the reaction of other phenolic compounds is reported as phenol. This value will represent the minimum concentration of phenolic compounds present in the sample.

3.3 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of less than 4.0 with H_2SO_4 and aerating briefly by stirring.

3.4 Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium

sulfate (see Paragraph 5.11). If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be low.

3.5 Phosphate causes a precipitate to form; therefore, phosphoric acid should not be used for preservation. All glassware should be phosphate free.

3.5 High concentrations of aldehydes may cause interferences.

4.0 APPARATUS AND MATERIALS

4.1 Distillation apparatus: All glass, consisting of a 1-liter Pyrex distilling apparatus with Graham condenser.

4.2 pH Meter.

4.3 Spectrophotometer.

4.4 Funnels.

4.5 Filter paper.

4.6 Membrane filters.

4.7 Separatory funnels.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Sulfuric acid, 1 N: Add 28 mL of concentrated H_2SO_4 to 900 mL of Type II water, mix, and dilute to 1 liter.

5.3 MBTH solution, 0.05%: Dissolve 0.1 g of 3-methyl-2-benzothiazolinone hydrazone hydrochloride in 200 mL of Type II water.

5.4 Ceric ammonium sulfate solution: Add 2.0 g of $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$ and 2.0 mL of concentrated H_2SO_4 to 150 mL of Type II water. After the solid has dissolved, dilute to 200 mL with Type II water.

5.5 Buffer solution: Dissolve, in the following order: 8 g of sodium hydroxide, 2 g EDTA (disodium salt), and 8 g boric acid in 200 mL of Type II water. Dilute to 250 mL with Type II water.

5.6 Working buffer solution: Make a working solution by mixing an appropriate volume of buffer solution (5.5) with an equal volume of ethanol.

5.7 Chloroform.

5.8 Stock phenol: Dissolve 1.00 g phenol in 500 mL of Type II water and dilute to 1,000 mL. Add 1 g $CuSO_4$ and 0.5 mL concentrated H_2SO_4 as preservative (1.0 mL = 1.0 mg phenol).

5.9 Standard phenol solution A: Dilute 10.0 mL of stock phenol solution (5.8) to 1,000 mL (1.0 mL = 0.01 mg phenol).

5.10 Standard phenol solution B: Dilute 100.0 mL of standard phenol solution A (5.9) to 1,000 mL with Type II water (1.0 mL = 0.001 mg phenol).

5.11 Ferrous ammonium sulfate: Dissolve 1.1 g ferrous ammonium sulfate in 500 mL Type II water containing 1 mL concentrated H_2SO_4 and dilute to 1 liter with freshly sorted and cooled Type II water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Biological degradation is inhibited by acidification to a pH of <4 with H_2SO_4. The sample should be kept at 4°C and analyzed within 28 days of collection.

7.0 PROCEDURE

7.1 Distillation:

7.1.1 To 500 mL of sample, adjust the pH to approximately 4 with 1 N sulfuric acid solution (5.2).

7.1.2 Distill over 450 mL of sample, add 50 mL of warm Type II water to flask, and resume distillation until 500 mL has been collected.

7.1.3 If the distillate is turbid, filter through a prewashed membrane filter.

7.2 Concentration above 50 ug/L:

7.2.1 To 100 mL of distillate or an aliquot diluted to 100 mL, add 4 mL of MBTH solution (5.3).

7.2.2 After 5 min, add 2.5 mL of ceric ammonium sulfate solution (5.4).

7.2.3 Wait another 5 min and add 7 mL of working buffer solution (5.6).

7.2.4 After 15 min, read the absorbance at 520 nm against a reagent blank. The color is stable for 4 hr.

7.3 Concentration below 50 ug/L:

7.3.1 To 500 mL of distillate in a separatory funnel, add 4 mL of MBTH solution (5.3).

7.3.2 After 5 min, add 2.5 mL of ceric ammonium sulfate solution (5.4).

7.3.3 After an additional 5 min, add 7 mL of working buffer solution (5.6).

7.3.4 After 15 min, add 25 mL of chloroform. Shake the separatory funnel at least 20 times. Allow the layer to separate and pass the chloroform layer through filter paper.

7.3.5 Read the absorbance at 490 nm against a reagent blank.

7.4 Calculation:

7.4.1 Prepare a standard curve by plotting absorbances against concentration values.

7.4.2 Obtain concentration value of sample directly from prepared standard curve.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

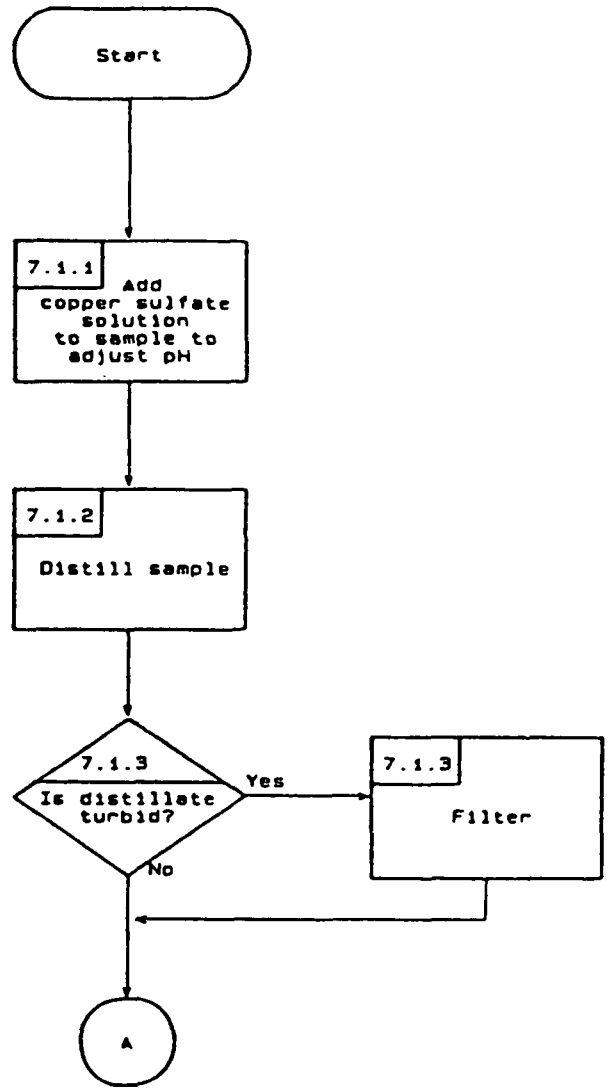
9.0 METHOD PERFORMANCE

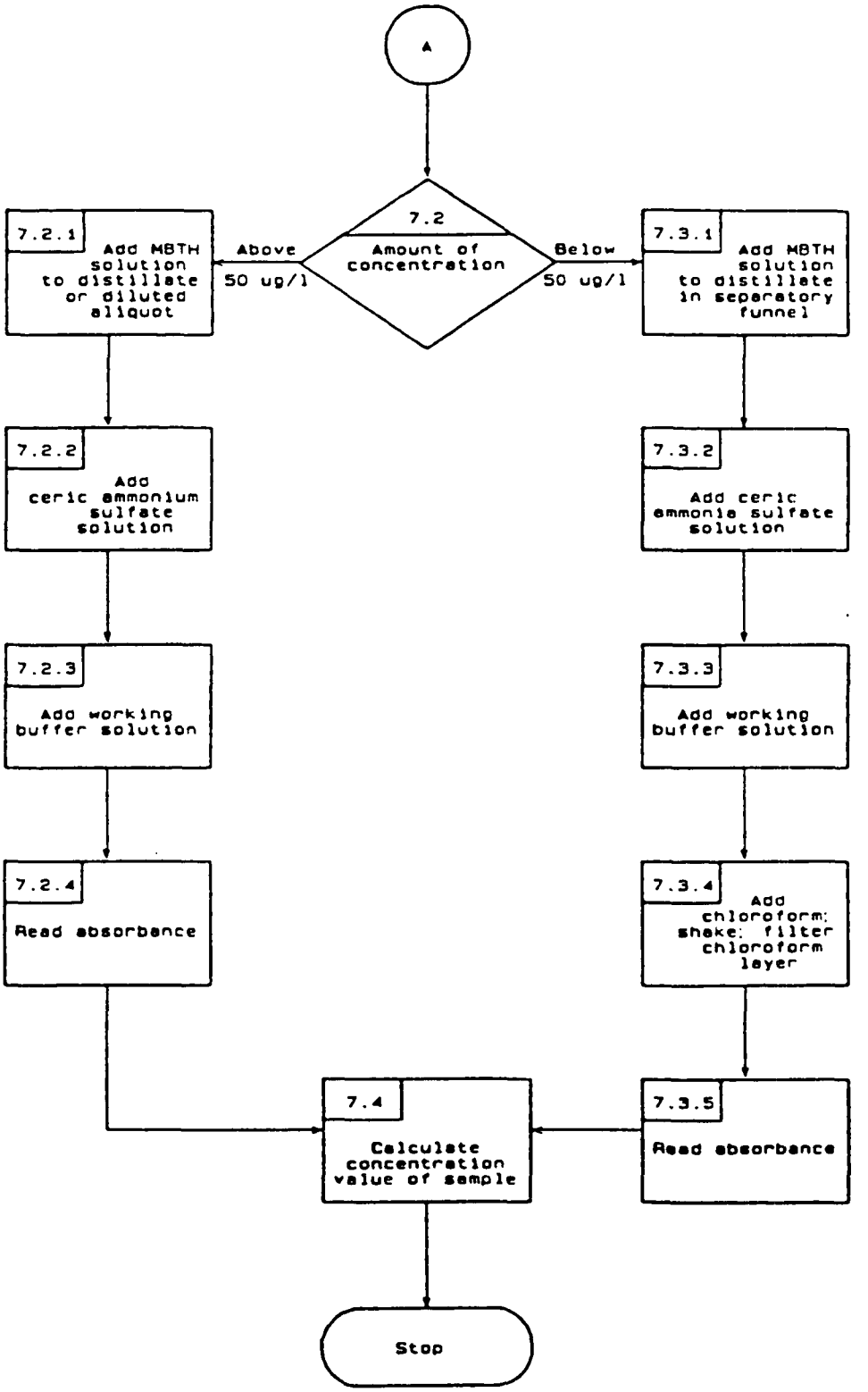
9.1 Precision and accuracy data are not available at this time.

10.0 REFERENCES

1. Friestad, H.O., E.E. Ott, and F.A. Gunther, "Automated Colorometric Micro Determination of Phenol by Oxidative Coupling with 3-Methyl-benzothiazolinone Hydrazone," Technicon International Congress, 1969.

2. Gales, M.E., "An Evaluation of the 3-Methyl-benzothiazolinone Hydrazone Method for the Determination of Phenols in Water and Wastewater," Analyst, 100, No. 1197, 841 (1975).


Start
7.1.1
Add copper sulfate solution to sample to adjust pH
7.1.2
Distill sample
7.1.3
Is distillate turbid?
Yes
No
7.1.3
Filter
A


A
7.2
Amount of concentration
Above 50 ug/l
Below 50 ug/l
7.2.1
Add MBTH solution to distillate or diluted aliquot
7.2.2
Add ceric ammonium sulfate solution
7.2.3
Add working buffer solution
7.2.4
Read absorbance
7.3.1
Add MBTH solution to distillate in separatory funnel
7.3.2
Add ceric ammonia sulfate solution
7.3.3
Add working buffer solution
7.3.4
Add chloroform; shake; filter chloroform layer
7.3.5
Read absorbance
7.4
Calculate concentration value of sample
Stop

TOTAL RECOVERABLE OIL AND GREASE (GRAVIMETRIC, SEPARATORY FUNNEL EXTRACTION)

1.0 SCOPE AND APPLICATION

1.1 This method measures the fluorocarbon-113 extractable matter from surface and saline waters and industrial, domestic, and aqueous wastes. It is applicable to the determination of relatively nonvolatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related matter.

1.2 The method is not applicable to measurement of light hydrocarbons that volatilize at temperatures below 70°C. Petroleum fuels, from gasoline through No. 2 fuel oils, are completely or partially lost in the solvent removal operation.

1.3 Some crude oils and heavy fuel oils contain a significant percentage of residue-type materials that are not soluble in fluorocarbon-113. Accordingly, recoveries of these materials will be low.

1.4 The method covers the range from 5 to 1,000 mg/L of extractable material.

1.5 When determining the level of oil and grease in sludge samples, Method 9071 is to be employed.

2.0 SUMMARY OF METHOD

2.1 The 1-liter sample is acidified to a low pH (2) and serially extracted with fluorocarbon-113 in a separatory funnel. The solvent is evaporated from the extract and the residue is weighed.

3.0 INTERFERENCES

3.1 Matrix interferences will likely be coextracted from the sample. The extent of these interferences will vary from waste to waste, depending on the nature and diversity of the waste being analyzed.

4.0 APPARATUS AND MATERIALS

4.1 Separatory funnel: 2,000-mL, with Teflon stopcock.

4.2 Vacuum pump, or other source of vacuum.

4.3 Flask: Boiling, 125-mL (Corning No. 4100 or equivalent).

4.4 Distilling head: Claisen or equivalent.

4.5 Filter paper: Whatman No. 40, 11 cm.

5.0 REAGENTS

5.1 Hydrochloric acid, 1:1: Mix equal volumes of concentrated HCl and Type II water.

5.2 Fluorocarbon-113 (1,1,2-trichloro-1,2,2-trifluoroethane): Boiling point, 48°C.

5.3 Sodium sulfate: Anhydrous crystal.

5.4 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 A representative sample should be collected in a 1-liter glass bottle. If analysis is to be delayed for more than a few hours, the sample is preserved by the addition of 5 mL HCl (5.1) at the time of collection and refrigerated at 4°C.

6.2 Collect a representative sample in a wide-mouth glass bottle that has been rinsed with the solvent to remove any detergent film and acidify in the sample bottle.

6.3 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.4 Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.

7.0 PROCEDURE

7.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 mL HCl (5.1) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to ensure that the pH is 2 or lower. Add more acid if necessary.

7.2 Pour the sample into a separatory funnel.

7.3 Tare a boiling flask (pre-dried in an oven at 103° and stored in a desiccator). Use gloves when handling flask to avoid adding fingerprints.

7.4 Add 30 mL fluorocarbon-113 (5.2) to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 min. Allow the layers to separate and filter the solvent layer through a funnel containing solvent-moistened filter paper.

NOTE: An emulsion that fails to dissipate can be broken by pouring about 1 g sodium sulfate (5.3) into the filter paper cone and slowly draining the emulsion through the salt. Additional 1-g portions can be added to the cone as required.

7.5 Repeat Step 7.4 twice more, with additional portions of fresh solvent, combining all solvent in the boiling flask.

7.6 Rinse the tip of the separatory funnel, the filter paper, and then the funnel with a total of 10-20 mL solvent and collect the rinsings in the flask.

7.7 Connect the boiling flask to the distilling head and evaporate the solvent by immersing the lower half of the flask in water at 70°C. Collect the solvent for reuse. A solvent blank should accompany each set of samples.

7.8 When the temperature in the distilling head reaches 50°C or the flask appears dry, remove the distilling head. To remove solvent vapor, sweep out the flask for 15 sec with air by inserting a glass tube that is connected to a vacuum source. Immediately remove the flask from heat source and wipe the outside to remove excess moisture and fingerprints.

7.9 Cool the boiling flask in a desiccator for 30 min and weigh.

7.10 Calculation:

$$\text{mg/L total oil and grease} = \frac{R - B}{V}$$

where:

R = residue, gross weight of extraction flask minus the tare weight;

B = blank determination, residue of equivalent volume of extraction solvent, mg; and

V = volume of sample in liters, determined by refilling sample bottle to calibration line and correcting for acid addition, if necessary.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.3 Verify calibration with an independently prepared check standard every 15 samples.

8.4 Run one spike duplicate sample for every 10 samples if possible. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

9.1 The two oil and grease methods (Methods 9070 and 9071) in this manual were tested on sewage by a single laboratory. This method determined the oil and grease level in the sewage to be 12.6 mg/L. When 1-liter portions of the sewage were dosed with 14.0 mg of a mixture of No. 2 fuel oil and Wesson oil, the recovery was 93%, with a standard deviation of $\pm$0.9 mg/L.

10.0 REFERENCES

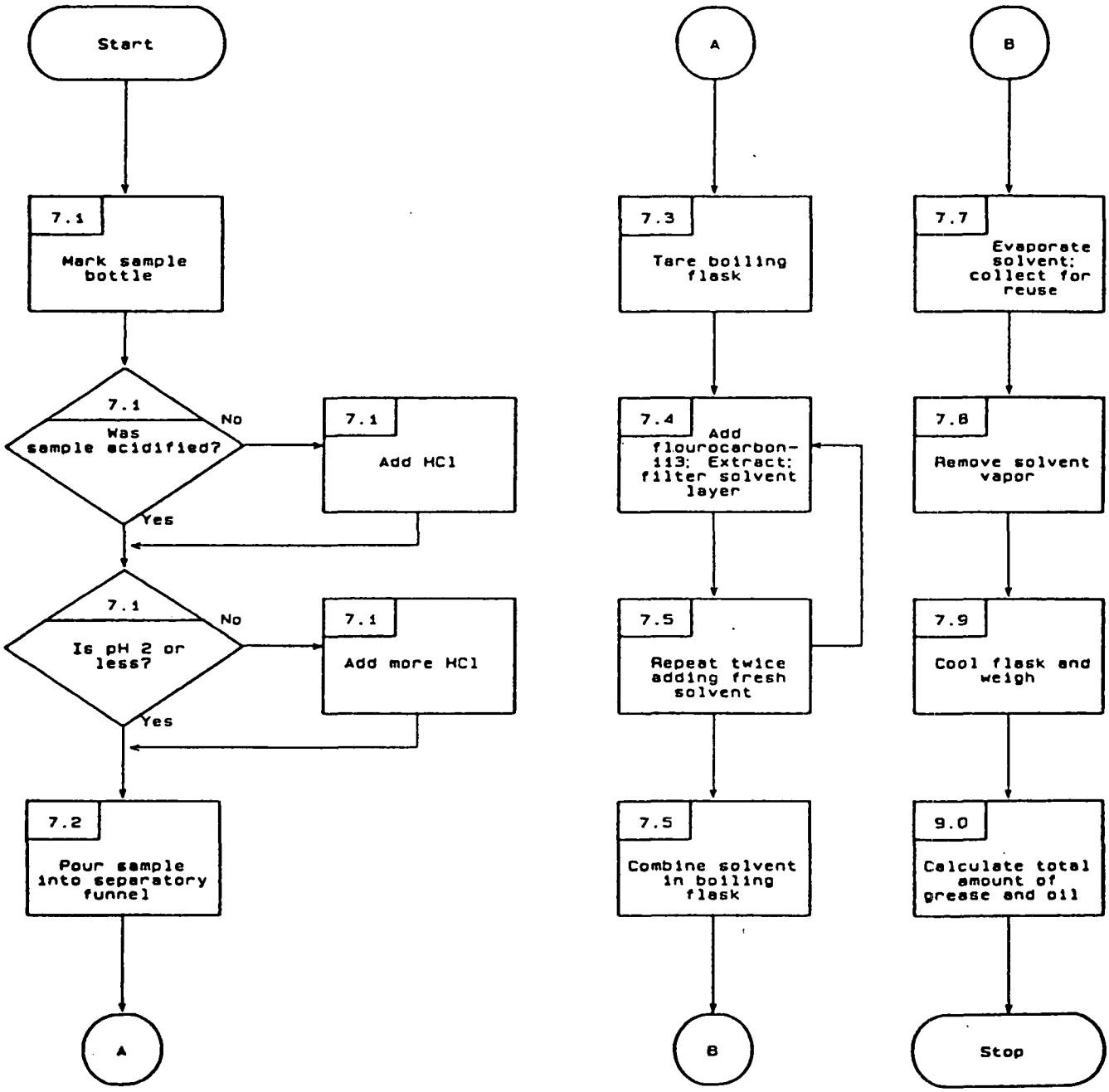
1. Blum, K.A., and M.J. Taras, "Determination of Emulsifying Oil in Industrial Wastewater," JWPCF Research Suppl., 40, R404 (1968).

2. Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 515.

METHOD 9070

TOTAL RECOVERABLE OIL AND GREASE

(Gravimetric, Separatory Funnel Extraction)



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METHOD 9071A

OIL AND GREASE EXTRACTION METHOD FOR SLUDGE AND SEDIMENT SAMPLES

1.0 SCOPE AND APPLICATION

1.1 Method 9071 is used to quantify low concentrations of oil and grease (10 mg/L) by chemically drying a wet sludge sample and then extracting via the Soxhlet apparatus. It is also used to recover oil and grease levels in sediment and soil samples.

1.2 Method 9071 is used when relatively polar, heavy petroleum fractions are present, or when the levels of nonvolatile greases challenge the solubility limit of the solvent.

1.3 Specifically, Method 9071 is suitable for biological lipids, mineral hydrocarbons, and some industrial wastewaters.

1.4 Method 9071 is not recommended for measurement of low-boiling fractions that volatilize at temperatures below 70°C.

2.0 SUMMARY OF METHOD

2.1 A 20-g sample of wet sludge with a known dry-solids content is acidified to pH 2.0 with 0.3 mL concentrated HCl.

2.2 Magnesium sulfate monohydrate will combine with 75% of its own weight in water in forming $MgSO_4 \cdot 7H_2O$ and is used to dry the acidified sludge sample.

2.3 Anhydrous sodium sulfate is used to dry samples of soil and sediment.

2.4 After drying, the oil and grease are extracted with trichlorotrifluoroethane (Fluorocarbon-113)[1] using the Soxhlet apparatus.

3.0 INTERFERENCES

3.1 The method is entirely empirical, and duplicate results can be obtained only by strict adherence to all details of the processes.

3.2 The rate and time of extraction in the Soxhlet apparatus must be exactly as directed because of varying solubilities of the different greases.

3.3 The length of time required for drying and cooling extracted material must be constant.

3.4 A gradual increase in weight may result due to the absorption of oxygen; a gradual loss of weight may result due to volatilization.

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[1]Replacement solvent will be specified in a forthcoming regulation.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extraction apparatus.

4.2 Analytical balance.

4.3 Vacuum pump or some other vacuum source.

4.4 Extraction thimble: Filter paper.

4.5 Glass wool or small glass beads to fill thimble.

4.6 Grease-free cotton: Extract nonabsorbent cotton with solvent.

4.7 Beaker: 150-mL.

4.8 pH Indicator to determine acidity.

4.9 Porcelain mortar.

4.10 Extraction flask: 150-mL.

4.11 Distilling apparatus: Waterbath at 70°C.

4.12 Desiccator.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Concentrated hydrochloric acid (HCl).

5.4 Magnesium sulfate monohydrate: Prepare $MgSO_4 \cdot H_2O$ by spreading a thin layer in a dish and drying in an oven at 150°C overnight.

5.5 Sodium sulfate, granular, anhydrous (Na_2SO_4): Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.6 Trichlorotrifluoroethane (1,1,2-trichloro-1,2,2-trifluoroethane): Boiling point, 47°C. The solvent should leave no measurable residue on evaporation; distill if necessary.[2]

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Transfers of the solvent trichlorotrifluoroethane should not involve any plastic tubing in the assembly.

6.2 Sample transfer implements: Implements are required to transfer portions of solid, semisolid, and liquid wastes from sample containers to laboratory glassware. Liquids may be transferred using a glass hypodermic syringe. Solids may be transferred using a spatula, spoon, or coring device.

6.3 Any turbidity or suspended solids in the extraction flask should be removed by filtering through grease-free cotton or glass wool.

7.0 PROCEDURE

7.1 Determination of Sample Dry Weight Fraction

Weigh 5-10 g of the sample into a tared crucible. Determine the dry weight fraction of the sample by drying overnight at 105°C.

> NOTE: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

Allow to cool in a desiccator before weighing:

$$\text{dry weight fraction} = \frac{\text{g of dry sample}}{\text{g of sample}}$$

7.2 Sample Handling

7.2.1 Sludge Samples

7.2.1.1 Weigh out 20 $\pm$ 0.5 g of wet sludge with a known dry-weight fraction (Section 7.1). Place in a 150-mL beaker.

7.2.1.2 Acidify to a pH of 2 with approximately 0.3 mL concentrated HCl.

7.2.1.3 Add 25 g prepared $Mg_2SO4 \cdot H_2O$ and stir to a smooth paste.

7.2.1.4 Spread paste on sides of beaker to facilitate evaporation. Let stand about 15-30 min or until substance is solidified.

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[2]Replacement solvent will be specified in a forthcoming regulation.

7.2.1.5 Remove solids and grind to fine powder in a mortar.

7.2.1.6 Add the powder to the paper extraction thimble.

7.2.1.7 Wipe beaker and mortar with pieces of filter paper moistened with solvent and add to thimble.

7.2.1.8 Fill thimble with glass wool (or glass beads).

7.2.2 Sediment/Soil Samples

7.2.2.1 Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.2.2.2 Blend 10 g of the solid sample of known dry weight fraction with 10 g of anhydrous sodium sulfate, and place in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period.

7.3 Extraction

7.3.1 Extract in Soxhlet apparatus using trichlorotrifluorocarbon at a rate of 20 cycles/hr for 4 hr.

7.3.2 Using grease-free cotton, filter the extract into a pre-weighed 250-mL boiling flask. Use gloves to avoid adding fingerprints to the flask.

7.3.3 Rinse flask and cotton with solvent.

7.3.4 Connect the boiling flask to the distilling head and evaporate the solvent by immersing the lower half of the flask in water at 70°C. Collect the solvent for reuse. A solvent blank should accompany each analytical batch of samples.

7.3.5 When the temperature in the distilling head reaches 50°C or the flask appears dry, remove the distilling head. To remove solvent vapor, sweep out the flask for 15 sec with air by inserting a glass tube that is connected to a vacuum source. Immediately remove the flask from the heat source and wipe the outside to remove excess moisture and fingerprints.

7.3.6 Cool the boiling flask in a desiccator for 30 min and weigh.

7.3.7 Calculate oil and grease as a percentage of the total dry solids. Generally:

$$\% \text{ of oil and grease} = \frac{\text{gain in weight of flask (g)} \times 100}{\text{wt. of wet solids (g)} \times \text{dry weight fraction}}$$

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference and inspection. Refer to Chapter One for additional quality control guidelines.

8.2 Employ a minimum of one blank per analytical batch or twenty samples, whichever is more frequent, to determine if contamination has occurred.

8.3 Run one matrix duplicate and matrix spike sample every twenty samples or analytical batch, whichever is more frequent. Matrix duplicates and spikes are brought through the whole sample preparation and analytical process.

8.4 The use of corn oil is recommended as a reference sample solution.

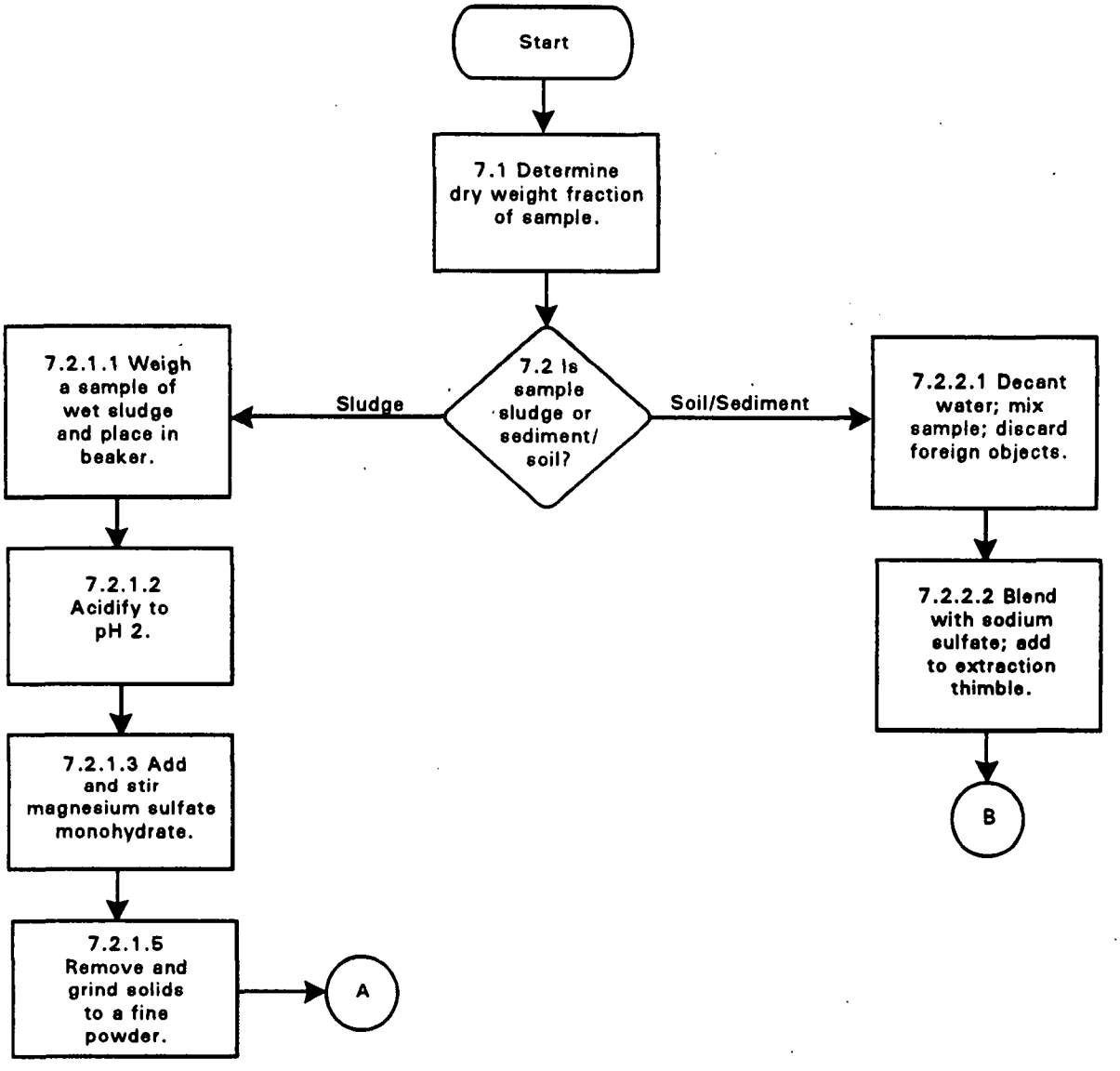
9.0 METHOD PERFORMANCE

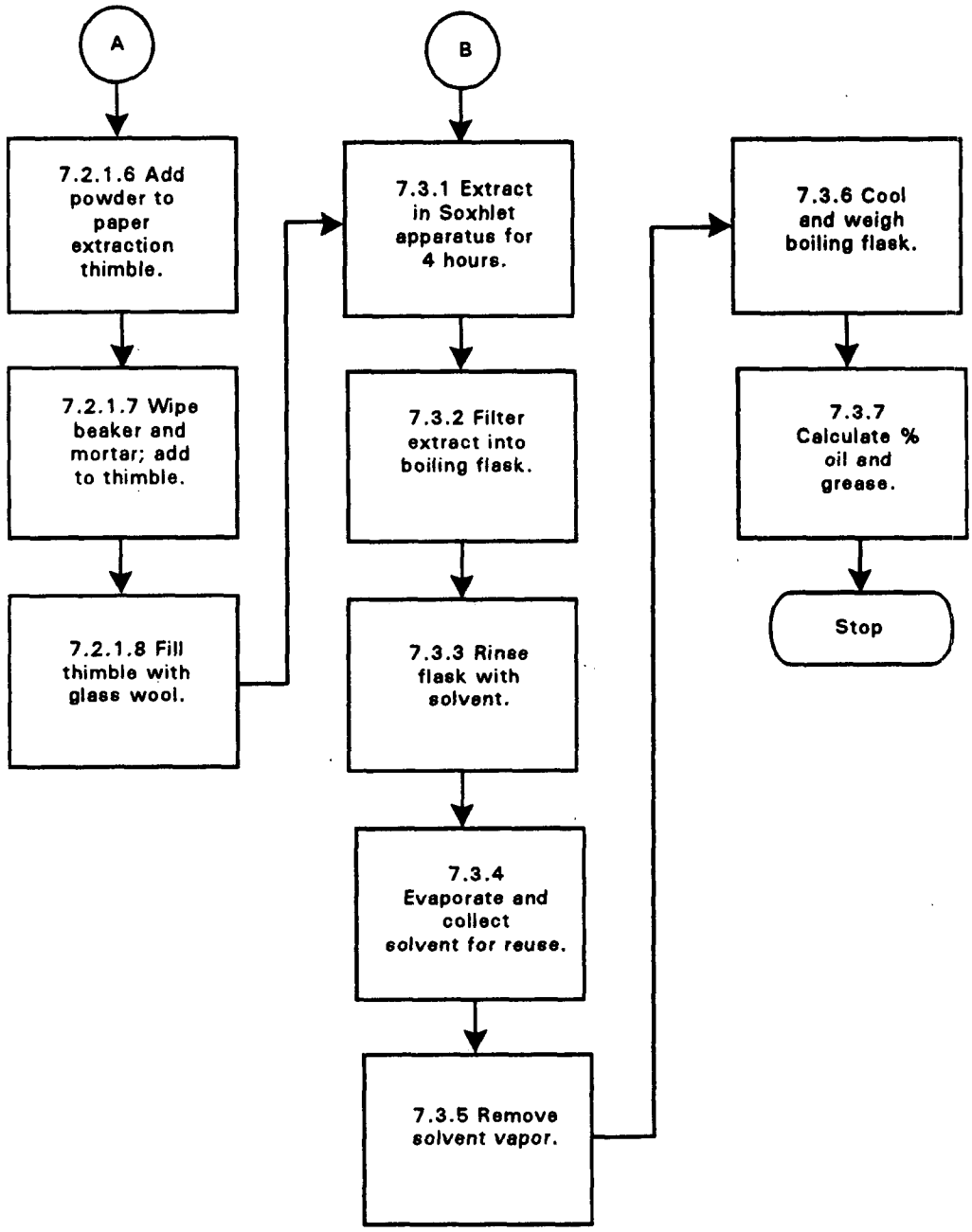
9.1 Two oil and grease methods (Methods 9070 and 9071) were tested on sewage by a single laboratory. When 1-liter portions of the sewage were dosed with 14.0 mg of a mixture of No. 2 fuel oil and Wesson oil, the recovery was 93%, with a standard deviation of $\pm$ 0.9 mg/L.

10.0 REFERENCES

1. Blum, K.A. and M.J. Taras, "Determination of Emulsifying Oil in Industrial Wastewater," JWPCF Research Suppl., 40, R404 (1968).

2. Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 515, Method 502A (1975).


Start
7.1 Determine dry weight fraction of sample.
7.2 Is sample sludge or sediment/ soil?
Sludge
Soil/Sediment
7.2.1.1 Weigh a sample of wet sludge and place in beaker.
7.2.1.2 Acidify to pH 2.
7.2.1.3 Add and stir magnesium sulfate monohydrate.
7.2.1.5 Remove and grind solids to a fine powder.
A
7.2.2.1 Decant water; mix sample; discard foreign objects.
7.2.2.2 Blend with sodium sulfate; add to extraction thimble.
B


A
B
7.2.1.6 Add powder to paper extraction thimble.
7.2.1.7 Wipe beaker and mortar; add to thimble.
7.2.1.8 Fill thimble with glass wool.
7.3.1 Extract in Soxhlet apparatus for 4 hours.
7.3.2 Filter extract into boiling flask.
7.3.3 Rinse flask with solvent.
7.3.4 Evaporate and collect solvent for reuse.
7.3.5 Remove solvent vapor.
7.3.6 Cool and weigh boiling flask.
7.3.7 Calculate % oil and grease.
Stop

METHOD 9075

TEST METHOD FOR TOTAL CHLORINE IN NEW AND USED PETROLEUM PRODUCTS BY X-RAY FLUORESCENCE SPECTROMETRY (XRF)

1.0 SCOPE AND APPLICATION

1.1 This test method covers the determination of total chlorine in new and used oils, fuels, and related materials, including crankcase, hydraulic, diesel, lubricating and fuel oils, and kerosene. The chlorine content of petroleum products is often required prior to their use as a fuel.

1.2 The applicable range of this method is from 200 μg/g to percent levels.

1.3 Method 9075 is restricted to use by, or under the supervision of, analysts experienced in the operation of an X-ray fluorescence spectrometer and in the interpretation of the results.

2.0 SUMMARY OF METHOD

2.1 A well-mixed sample, contained in a disposable plastic sample cup, is loaded into an X-ray fluorescence (XRF) spectrometer. The intensities of the chlorine Kα and sulfur Kα lines are measured, as are the intensities of appropriate background lines. After background correction, the net intensities are used with a calibration equation to determine the chlorine content. The sulfur intensity is used to correct for absorption by sulfur.

3.0 INTERFERENCES

3.1 Possible interferences include metals, water, and sediment in the oil. Results of spike recovery measurements and measurements on diluted samples can be used to check for interferences.

Each sample, or one sample from a group of closely related samples, should be spiked to confirm that matrix effects are not significant. Dilution of samples that may contain water or sediment can produce incorrect results, so dilution should be undertaken with caution and checked by spiking. Sulfur interferes with the chlorine determination, but a correction is made.

Spike recovery measurements of used crankcase oil showed that diluting samples five to one allowed accurate measurements on approximately 80% of the samples. The other 20% of the samples were not accurately analyzed by XRF.

3.2 Water in samples absorbs X-rays emmitted by chlorine. For this inter-ference, use of as short an X-ray counting time as possible is beneficial. This appears to be related to stratification of samples into aqueous and nonaqueous layers while in the analyzer.

Although a correction for water may be possible, none is currently available. In general, the presence of any free water as a separate phase or a

water content greater than 25% will reduce the chlorine signal by 50 to 90%. See Sec. 6.4.

4.0 APPARATUS AND MATERIALS

4.1 XRF spectrometer, either energy dispersive or wavelength dispersive. The instrument must be able to accurately resolve and measure the intensity of the chlorine and sulfur lines with acceptable precision.

4.2 Disposable sample cups with suitable plastic film such as Mylar®.

5.0 REAGENTS

5.1 Purity of reagents. Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Mineral oil, mineral spirits or paraffin oil (sulfur- and chlorine-free), for preparing standards and dilutions.

5.3 1-Chlorodecane (Aldrich Chemical Co.), 20.1% chlorine, or similar chlorine compound.

5.4 Di-n-butyl sulfide (Aldrich Chemical Co.), 21.9% sulfur by weight.

5.5 Quality control standards such as the standard reference materials NBS 1620, 1621, 1622, 1623, and 1624 for sulfur in oil standards; and NBS 1818 for chlorine in oil standards.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 The collected sample should be kept headspace free prior to preparation and analysis to minimize volatilization losses of organic halogens. Because waste oils may contain toxic and/or carcinogenic substances, appropriate field and laboratory safety procedures should be followed.

6.3 Laboratory sampling of the sample should be performed on a well-mixed sample of oil. The mixing should be kept to a minimum and carried out as nearly headspace free as possible to minimize volatilization losses of organic halogens.

6.4 Free water, as a separate phase, should be removed and cannot be analyzed by this method.

7.0 PROCEDURE

7.1 Calibration and standardization.

7.1.1 Prepare primary calibration standards by diluting the chlorodecane and n-butyl sulfide with mineral spirits or similar material.

7.1.2 Prepare working calibration standards that contain sulfur, chlorine, or both according to the following table:

Cl: 500, 1,000, 2,000, 4,000, and 6,000 μg/g
S: 0.5, 1.0, and 1.5% sulfur

1.	0.5% S, 1,000 μg/g Cl	5.	1.0% S, 6,000 μg/g Cl
2.	0.5% S, 4,000 μg/g Cl	6.	1.5% S, 1,000 μg/g Cl
3.	1.0% S, 500 μg/g Cl	7.	1.5% S, 4,000 μg/g Cl
4.	1.0% S, 2,000 μg/g Cl	8.	1.5% S, 6,000 μg/g Cl

Once the correction factor for sulfur interference with chlorine is determined, fewer standards may be required.

7.1.3 Measure the intensity of the chlorine Kα line and the sulfur Kα line as well as the intensity of a suitably chosen background. Based on counting statistics, the relative standard deviation of each peak measurement should be 1% or less.

7.1.4 Determine the net chlorine and sulfur intensities by correcting each peak for background. Do this for all of the calibration standards as well as for a paraffin blank.

7.1.5 Obtain a linear calibration curve for sulfur by performing a least squares fit of the net sulfur intensity to the standard concentrations, including the blank. The chlorine content of a standard should have little effect on the net sulfur intensity.

7.1.6 The calibration equation for chlorine must include a correction term for the sulfur concentration. A suitable equation follows:

$$Cl = (mI + b)\ (1 + k^*S) \qquad (1)$$

where:

I = net chlorine intensity
m, b, k* = adjustable parameters
S = sulfer concentration

Using a least squares procedure, the above equation or a suitable substitute should be fitted to the data. Many XRF instruments are equipped with suitable computer programs to perform this fit. In any case, the resulting equation should be shown to be accurate by analysis of suitable standard materials.

7.2 Analysis.

7.2.1 Prepare a calibration curve as described in Sec. 7.1. By periodically measuring a very stable sample containing both sulfur and chlorine, it may be possible to use the calibration equations for more than 1 day. During each day, the suitability of the calibration curve should be checked by analyzing standards.

7.2.2 Determine the net chlorine and sulfur intensities for a sample in the same manner as done for the standards.

7.2.3 Determine the chlorine and sulfur concentrations of the samples from the calibration equations. If the sample concentration for either element is beyond the range of the standards, the sample should be diluted with mineral oil and reanalyzed.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 One sample in ten should be analyzed in triplicate and the relative standard deviation reported. For each triplicate, a separate preparation should be made, starting from the original sample.

8.3 Each sample, or one sample in ten from a group of similar samples, should be spiked with the elements of interest by adding a known amount of chlorine or sulfur to the sample. The spiked amount should be between 50% and 200% of the sample concentration, but the minimum addition should be at least five times the limit of detection. The percent recovery should be reported and should be between 80% and 120%. Any sample suspected of containing >25% water should also be spiked with organic chlorine.

8.4 Quality control standard check samples should be analyzed every day and should agree within 10% of the expected value of the standard.

9.0 METHOD PERFORMANCE

9.1 These data are based on 47 data points obtained by seven laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. A data point represents one duplicate analysis of a sample. Two data points were determined to be outliers and are not included in these results.

9.2 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 1):

$$Repeatability = 5.72 \sqrt{x}*$$

*where x is the average of two results in μg/g.

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$Reproducibility = 9.83 \sqrt{x}*$$

*where x is the average value of two results in μg/g.

9.3 Bias. The bias of this test method varies with concentration, as shown in Table 2:

Bias = Amount found - Amount expected.

10.0 REFERENCE

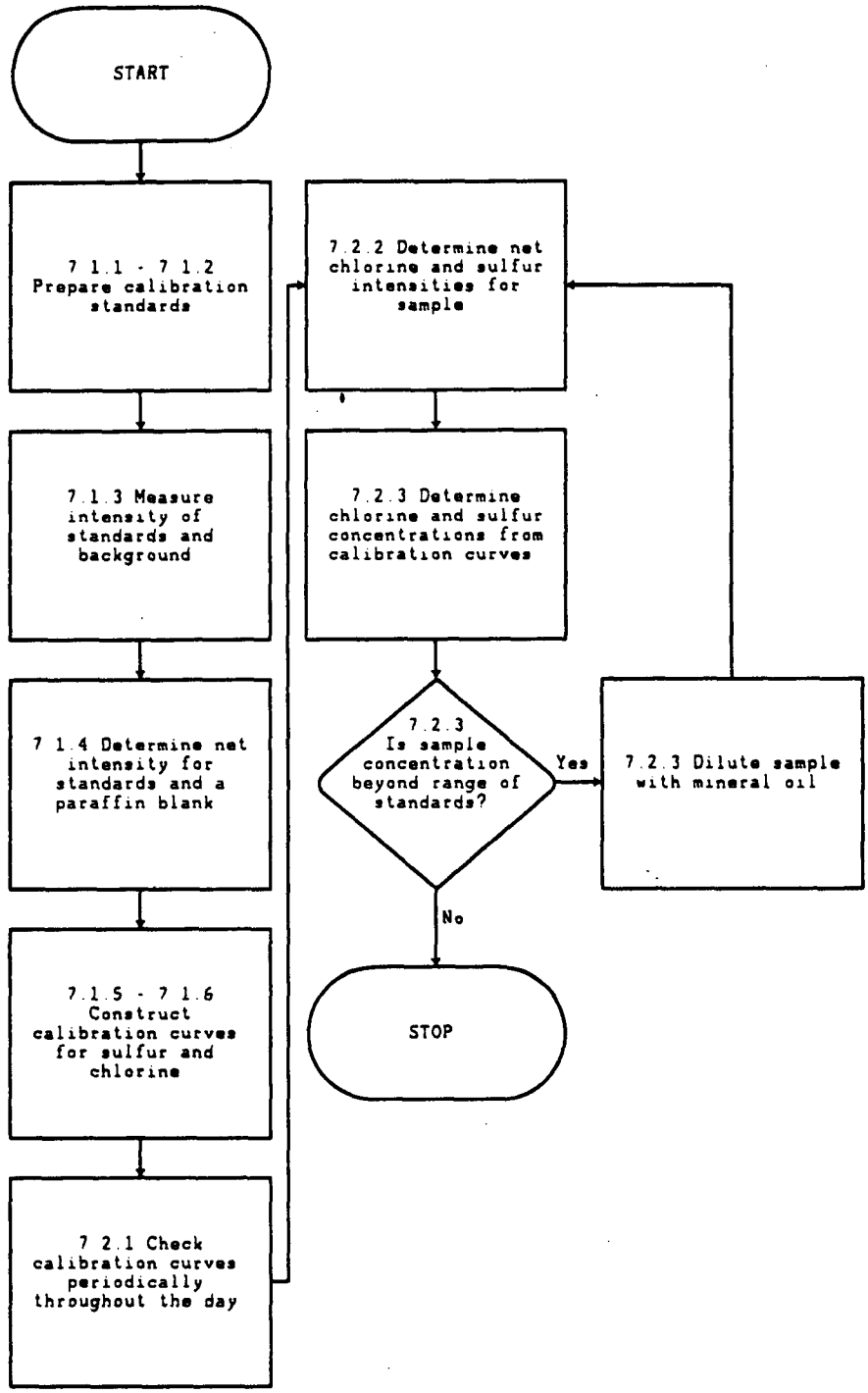
1. Gaskill, A.; Estes, E.D.; Hardison, D.L.; and Myers, L.E. Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels. Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA 80. July 1988.

TABLE 1. REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED OILS BY X-RAY FLUORESCENCE SPECTROMETRY

Average value, µg/g	Repeatability, µg/g	Reproducibility, µg/g
500	128	220
1,000	181	311
1,500	222	381
2,000	256	440
2,500	286	492
3,000	313	538

TABLE 2. RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY X-RAY FLUORESCENCE SPECTROMETRY

Amount expected, µg/g	Amount found, µg/g	Bias, µg/g	Percent bias
320	278	-42	-13
480	461	-19	-4
920	879	-41	-4
1,498	1,414	-84	-6
1,527	1,299	-228	-15
3,029	2,806	-223	-7
3,045	2,811	-234	-8


START
7.1.1 - 7.1.2 Prepare calibration standards
7.1.3 Measure intensity of standards and background
7.1.4 Determine net intensity for standards and a paraffin blank
7.1.5 - 7.1.6 Construct calibration curves for sulfur and chlorine
7.2.1 Check calibration curves periodically throughout the day
7.2.2 Determine net chlorine and sulfur intensities for sample
7.2.3 Determine chlorine and sulfur concentrations from calibration curves
7.2.3 Is sample concentration beyond range of standards?
Yes
7.2.3 Dilute sample with mineral oil
No
STOP

METHOD 9076

TEST METHOD FOR TOTAL CHLORINE IN NEW AND USED PETROLEUM PRODUCTS BY OXIDATIVE COMBUSTION AND MICROCOULOMETRY

1.0 SCOPE AND APPLICATION

1.1 This test method covers the determination of total chlorine in new and used oils, fuels and related materials, including crankcase, hydraulic, diesel, lubricating and fuel oils, and kerosene by oxidative combustion and microcoulometry. The chlorine content of petroleum products is often required prior to their use as a fuel.

1.2 The applicable range of this method is from 10 to 10,000 $\mu g/g$ chlorine.

2.0 SUMMARY OF METHOD

2.1 The sample is placed in a quartz boat at the inlet of a high-temperature quartz combustion tube. An inert carrier gas such as argon, carbon dioxide, or nitrogen sweeps across the inlet while oxygen flows into the center of the combustion tube. The boat and sample are advanced into a vaporization zone of approximately 300°C to volatilize the light ends. Then the boat is advanced to the center of the combustion tube, which is at 1,000°C. The oxygen is diverted to pass directly over the sample to oxidize any remaining refractory material. All during this complete combustion cycle, the chlorine is converted to chloride and oxychlorides, which then flow into an attached titration cell where they quantitatively react with silver ions. The silver ions thus consumed are coulometrically replaced. The total current required to replace the silver ions is a measure of the chlorine present in the injected samples.

2.2 The reaction occurring in the titration cell as chloride enters is:

$$Cl^- + Ag^+ \text{ -------> } AgCl \qquad (1)$$

The silver ion consumed in the above reaction is generated coulometrically thus:

$$Ag^\circ \text{ -------> } Ag^+ + e^- \qquad (2)$$

2.3 These microequivalents of silver are equal to the number of microequivalents of titratable sample ion entering the titration cell.

3.0 INTERFERENCES

3.1 Other titratable halides will also give a positive response. These titratable halides include HBr and HI (HOBr + HOI do not precipitate silver). Because these oxyhalides do not react in the titration cell, approximately 50% microequivalent response is detected from bromine and iodine.

3.2 Fluorine as fluoride does not precipitate silver, so it is not an interferant nor is it detected.

3.3 This test method is applicable in the presence of total sulfur concentrations of up to 10,000 times the chlorine level.

4.0 APPARATUS AND MATERIALS[1]

4.1 Combustion furnace. The sample should be oxidized in an electric furnace capable of maintaining a temperature of 1,000°C to oxidize the organic matrix.

4.2 Combustion tube, fabricated from quartz and constructed so that a sample, which is vaporized completely in the inlet section, is swept into the oxidation zone by an inert gas where it mixes with oxygen and is burned. The inlet end of the tube connects to a boat insertion device where the sample can be placed on a quartz boat by syringe, micropipet, or by being weighed externally. Two gas ports are provided, one for an inert gas to flow across the boat and one for oxygen to enter the combustion tube.

4.3 Microcoulometer, Stroehlein Coulomat 702 CL or equivalent, having variable gain and bias control, and capable of measuring the potential of the sensing-reference electrode pair, and comparing this potential with a bias potential, and applying the amplified difference to the working-auxiliary electrode pair so as to generate a titrant. The microcoulometer output signal shall be proportional to the generating current. The microcoulometer may have a digital meter and circuitry to convert this output signal directly to a mass of chlorine (e.g., nanograms) or to a concentration of chlorine (e.g., micrograms of chlorine or micrograms per gram).

4.4 Titration cell. Two different configurations have been applied to coulometrically titrate chlorine for this method.

4.4.1 Type I uses a sensor-reference pair of electrodes to detect changes in silver ion concentration and a generator anode-cathode pair of electrodes to maintain constant silver ion concentration and an inlet for a gaseous sample from the pyrolysis tube. The sensor, reference, and anode electrodes are silver electrodes. The cathode electrode is a platinum wire. The reference electrode resides in a saturated silver acetate half-cell. The electrolyte contains 70% acetic acid in water.

4.4.2 Type II uses a sensor-reference pair of electrodes to detect changes in silver ion concentration and a generator anode-cathode pair of electrodes to maintain constant silver ion concentration, an inlet for a gaseous sample that passes through a 95% sulfuric acid dehydrating tube from the pyrolysis tube, and a sealed two-piece titration cell with an exhaust tube to vent fumes to an external exhaust. All electrodes can be removed and replaced independently without reconstructing the cell assembly. The anode electrode is constructed of silver. The cathode electrode is constructed of platinum. The anode is separated from the

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[1]Any apparatus that meets the performance criteria of this section may be used to conduct analyses by this methodology. Three commercial analyzers that fulfill the requirements for apparatus Steps 4.1 through 4.4 are: Dohrmann Models DX-20B and MCTS-20 and Mitsubishi Model TSX-10 available from Cosa Instrument.

cathode by a 10% KNO_3 agar bridge, and continuity is maintained through an aqueous 10% KNO_3 salt bridge. The sensor electrode is constructed of silver. The reference electrode is a silver/silver chloride ground glass sleeve, double-junction electrode with aqueous 1M KNO_3 in the outer chamber and aqueous 1M KCl in the inner chamber.

4.5 Sampling syringe, a microliter syringe of 10 μL capacity capable of accurately delivering 2 to 5 μL of a viscous sample into the sample boat.

4.6 Micropipet, a positive displacement micropipet capable of accurately delivering 2 to 5 μL of a viscous sample into the sample boat.

4.7 Analytical balance. When used to weigh a sample of 2 to 5 mg onto the boat, the balance shall be accurate to $\pm$ 0.01 mg. When used to determine the density of the sample, typically 8 g per 10 mL, the balance shall be accurate to $\pm$ 0.1 g.

4.8 Class A volumetric flasks: 100 mL.

5.0 REAGENTS

5.1 Purity of Reagents. Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Acetic acid, CH_3CO_2H. Glacial.

5.4 Isooctane, $(CH_3)_2CHCH_2C(CH_3)_3$ (2,2,4-Trimethylpentane).

5.5 Chlorobenzene, C_6H_5Cl.

5.6 Chlorine, standard stock solution - 10,000 ng Cl/μL, weigh accurately 3.174 g of chlorobenzene into 100-mL Class A volumetric flask. Dilute to the mark with isooctane.

5.7 Chlorine, standard solution. 1,000 ng Cl/μL, pipet 10.0 mL of chlorine stock solution (Sec. 5.6) into a 100-mL volumetric flask and dilute to volume with isooctane.

5.8 Argon, helium, nitrogen, or carbon dioxide, high-purity grade (HP) used as the carrier gas. High-purity grade gas has a minimum purity of 99.995%.

5.9 Oxygen, high-purity grade (HP), used as the reactant gas.

5.10 Gas regulators. Two-stage regulator must be used on the reactant and carrier gas.

5.11 Cell Type 1.

5.11.1 Cell electrolyte solution. 70% acetic acid: combine 300 mL reagent water with 700 mL acetic acid (Sec. 5.3) and mix well.

5.11.2 Silver acetate, CH_3CO_2Ag. Powder purified for saturated reference electrode.

5.12 Cell Type 2.

5.12.1 Sodium acetate, CH_3CO_2Na.

5.12.2 Potassium nitrate, KNO_3.

5.12.3 Potassium chloride, KCl.

5.12.4 Sulfuric acid (concentrated), H_2SO_4.

5.12.5 Agar, (jelly strength 450 to 600 g/cm^2).

5.12.6 Cell electrolyte solution - 85% acetic acid: combine 150 mL reagent water with 1.35 g sodium acetate (Sec. 5.12.1) and mix well; add 850 mL acetic acid (Sec. 5.3) and mix well.

5.12.7 Dehydrating solution - Combine 95 mL sulfuric acid (Sec. 5.12.4) with 5 mL reagent water and mix well.

CAUTION: This is an exothermic reaction and may proceed with bumping unless controlled by the addition of sulfuric acid. Slowly add sulfuric acid to reagent water. Do not add water to sulfuric acid.

5.12.8 Potassium nitrate (10%), KNO_3. Add 10 g potassium nitrate (Sec. 5.12.2) to 100 mL reagent water and mix well.

5.12.9 Potassium nitrate (1M), KNO_3. Add 10.11 g potassium nitrate (Sec. 5.12.2) to 100 mL reagent water and mix well.

5.12.10 Potassium chloride (1M), KCl. Add 7.46 g potassium chloride (Sec. 5.12.3) to 100 mL reagent water and mix well.

5.12.11 Agar bridge solution - Mix 0.7 g agar (Sec. 5.12.5), 2.5g potassium nitrate (Sec. 5.12.2), and 25 mL reagent water and heat to boiling.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 Because the collected sample will be analyzed for total halogens, it should be kept headspace free and refrigerated prior to preparation and analysis to minimize volatilization losses of organic halogens. Because waste oils may

contain toxic and/or carcinogenic substances, appropriate field and laboratory safety procedures should be followed.

6.3 Laboratory subsampling of the sample should be performed on a well-mixed sample of oil.

7.0 PROCEDURES

7.1 Preparation of apparatus.

7.1.1 Set up the analyzer as per the equipment manufacturer's instructions.

7.1.2 Typical operating conditions: Type 1.

Furnace temperature	1,000°C
Carrier gas flow	43 cm^3/min
Oxygen gas flow	160 cm^3/min
Coulometer	
Bias	250 mV
Gain	25%

7.1.3 Typical operating conditions: Type 2.

Furnace temperature	H-1 850°C H-2 1,000°C
Carrier gas flow	250 cm^3/min
Oxygen gas flow	250 cm^3/min
Coulometer	
End point potential (bias)	300 mV
Gain G-1	1.5 coulombs/Δ mV
G-2	3.0 coulombs/Δ mV
G-3	3.0 coulombs/Δ mV
ES-1 (range 1)	25 mV
ES-2 (range 2)	30 mV

NOTE: Other conditions may be appropriate. Refer to the instrumentation manual.

7.2 Sample introduction.

7.2.1 Carefully fill a 10-μL syringe with 2 to 5 μL of sample depending on the expected concentration of total chlorine. Inject the sample through the septum onto the cool boat, being certain to touch the boat with the needle tip to displace the last droplet.

7.2.2 For viscous samples that cannot be drawn into the syringe barrel, a positive displacement micropipet may be used. Here, the 2-5 μL of sample is placed on the boat from the micropipet through the opened hatch port. The same technique as with the syringe is used to displace the last droplet into the boat. A tuft of quartz wool in the boat can aid in completely transferring the sample from the micropipet into the boat.

NOTE: Dilution of samples to reduce viscosity is not recommended due to uncertainty about the solubility of the sample and its chlorinated constituents. If a positive displacement micropipet is not available, dilution may be attempted to enable injection of viscous samples.

7.2.3 Alternatively, the sample boat may be removed from the instrument and tared on an analytical balance. A sample of 2-5 mg is accurately weighed directly into the boat and the boat and sample returned to the inlet of the instrument.

2-5 μL = 2-5 mg

NOTE: Sample dilution may be required to ensure that the titration system is not overloaded with chlorine. This will be somewhat system dependent and should be determined before analysis is attempted. For example, the MCTS-20 can titrate up to 10,000 ng chlorine in a single injection or weighed sample, while the DX-20B has an upper limit of 50,000 ng chlorine. For 2 to 5 μL sample sizes, these correspond to nominal concentrations in the sample of 800 to 2,000 μg/g and 4,000 to 10,000 μg/g, respectively. If the system is overloaded, especially with inorganic chloride, residual chloride may persist in the system and affect results of subsequent samples. In general, the analyst should ensure that the baseline returns to normal before running the next sample. To speed baseline recovery, the electrolyte can be drained from the cell and replaced with fresh electrolyte.

NOTE: To determine total chlorine, do not extract the sample either with reagent water or with an organic solvent such as toluene or isooctane. This may lower the inorganic chlorine content as well as result in losses of volatile solvents.

7.2.4 Follow the manufacturer's recommended procedure for moving the sample and boat into the combustion tube.

7.3 Calibration and standardization.

7.3.1 System recovery - The fraction of chlorine in a standard that is titrated should be verified every 4 hours by analyzing the standard solution (Sec. 5.7). System recovery is typically 85% or better. The pyrolysis tube should be replaced whenever system recovery drops below 75%.

NOTE: The 1,000 μg/g system recovery sample is suitable for all systems except the MCTS-20 for which a 100 μg/g sample should be used.

7.3.2 Repeat the measurement of this standard at least three times.

7.3.3 System blank - The blank should be checked daily with isooctane. It is typically less than 1 μg/g chlorine. The system blank should be subtracted from both samples and standards.

7.4 Calculations.

7.4.1 For systems that read directly in mass units of chloride, the following equations apply:

$$\text{Chlorine, } \mu g/g \text{ (wt/wt)} = \frac{\text{Display}_S}{(V_S)\ (D_S)\ (RF)} - B \qquad (3)$$

or

$$\text{Chlorine, } \mu g/g \text{ (wt/wt)} = \frac{\text{Display}_S}{(M)\ (RF)} - B \qquad (4)$$

where:

Display = Integrated value in nanograms (when the integrated values are displayed in micrograms, they must be multiplied by 10^3)
Display_B = blank measurement Display_S = sample measurement

V = Volume of sample injected in microliters
V_B = blank volume V_S = sample volume

D = Density of sample, grams per cubic centimeters
D_B = blank density D_S = sample density

RF = Recovery factor = ratio of chlorine determined in standard minus the system blank, divided by known standard content = $\frac{\text{Found - Blank}}{\text{Known}}$

B = System blank, μg/g chlorine = $\frac{\text{Display}_B}{(V_B)\ (D_B)}$

M = Mass of sample, mg

7.4.2 Other systems internally compensate for recovery factor, volume, density, or mass and blank, and thus read out directly in parts per million chlorine units. Refer to instrumentation manual.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Each sample should be analyzed twice. If the results do not agree to within 10%, expressed as the relative percent difference of the results, repeat the analysis.

8.3 Analyze matrix spike and matrix spike duplicates - spike samples with a chlorinated organic at a level of total chlorine commensurate with the levels being determined. The spike recovery should be reported and should be between

80 and 120% of the expected value. Any sample suspected of containing >25% water should also be spiked with organic chlorine.

9.0 METHOD PERFORMANCE

9.1 These data are based on 66 data points obtained by 10 laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. A data point represents one duplicate analysis of a sample. One laboratory and four additional data points were determined to be outliers and are not included in these results.

9.2 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method the following values only in 1 case in 20 (see Table 1):

$$Repeatability = 0.137\ x*$$

*where x is the average of two results in μg/g.

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$Reproducibility = 0.455\ x*$$

*where x is the average value of two results in μg/g.

9.3 Bias. The bias of this test method varies with concentration, as shown in Table 2:

Bias = Amount found - Amount expected

10.0 REFERENCE

1. Gaskill, A.; Estes, E.D.; Hardison, D.L.; and Myers, L.E. "Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels." Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA80. July 1988.

2. Rohrobough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

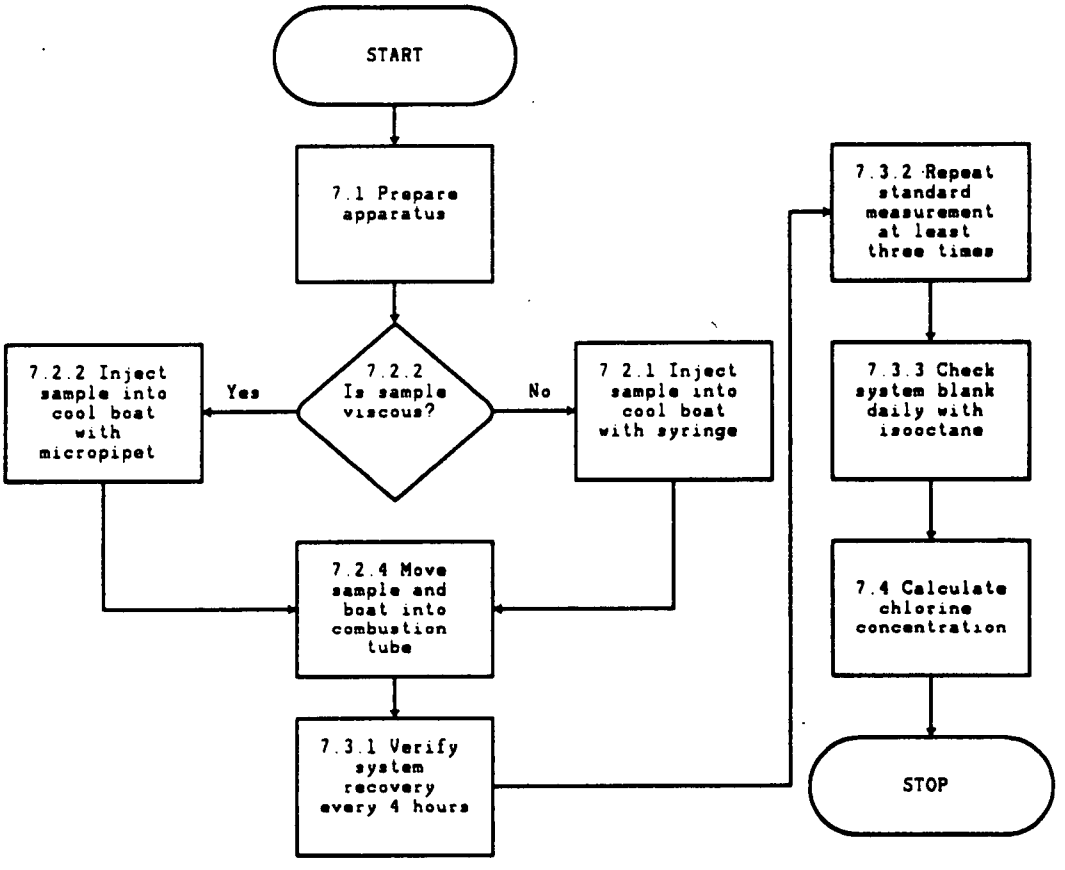
3. Standard Instrumentation, 3322 Pennsylvania Avenue, Charleston, WV 25302.

TABLE 1.
REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED OILS BY MICROCOULOMETRIC TITRATION

Average value µg/g	Repeatability, µg/g	Reproducibility, µg/g
500	69	228
1,000	137	455
1,500	206	683
2,000	274	910
2,500	343	1,138
3,000	411	1,365

TABLE 2.
RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY MICROCOULOMETRIC TITRATION

Amount expected, µg/g	Amount found µg/g	Bias, µg/g	Percent bias
320	312	-8	-3
480	443	-37	-8
920	841	-79	-9
1,498	1,483	-15	-1
1,527	1,446	-81	-5
3,029	3,016	-13	0
3,045	2,916	-129	-4


START
7.1 Prepare apparatus
7.2.2 Is sample viscous?
Yes
No
7.2.2 Inject sample into cool boat with micropipet
7.2.1 Inject sample into cool boat with syringe
7.2.4 Move sample and boat into combustion tube
7.3.1 Verify system recovery every 4 hours
7.3.2 Repeat standard measurement at least three times
7.3.3 Check system blank daily with isooctane
7.4 Calculate chlorine concentration
STOP

METHOD 9077

TEST METHODS FOR TOTAL CHLORINE IN NEW AND USED PETROLEUM PRODUCTS (FIELD TEST KIT METHODS)

1.0 SCOPE AND APPLICATION

1.1 The method may be used to determine if a new or used petroleum product meets or exceeds requirements for total halogen measured as chloride. An analysis of the chlorine content of petroleum products is often required prior to their use as a fuel. The method is specifically designed for used oils permitting onsite testing at remote locations by nontechnical personnel to avoid the delays for laboratory testing.

1.2 In these field test methods, the entire analytical sequence, including sampling, sample pretreatment, chemical reactions, extraction, and quantification, are combined in a single kit using predispensed and encapsulated reagents. The overall objective is to provide a simple, easy to use procedure, permitting nontechnical personnel to perform a test with analytical accuracy outside of a laboratory environment in under 10 minutes. One of the kits is preset at 1,000 μg/g total chlorine to meet regulatory requirements for used oils. The other kits provide quantitative results over a range of 750 to 7,000 μg/g and 300 to 4,000 μg/g.

2.0 SUMMARY OF METHOD

2.1 The oil sample (around 0.4 g by volume) is dispersed in a solvent and reacted with a mixture of metallic sodium catalyzed with naphthalene and diglyme at ambient temperature. This process converts all organic halogens to their respective sodium halides. All halides in the treated mixture, including those present prior to the reaction, are then extracted into an aqueous buffer, which is then titrated with mercuric nitrate using diphenyl carbazone as the indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex. Bromide and iodide are titrated and reported as chloride.

2.2 Reagent quantities are preset in the fixed end point kit (Method A) so that the color of the solution at the end of the titration indicates whether the sample is above 1,000 μg/g chlorine (yellow) or below 1,000 μg/g chlorine (blue).

2.3 The first quantitative kit (Method B) involves a reverse titration of a fixed volume of mercuric nitrate with the extracted sample such that the end point is denoted by a change from blue to yellow in the titration vessel over the range of the kit (750 to 7,000 μg/g). The final calculation is based on the assumption that the oil has a specific gravity of 0.9 g/cm^3.

2.4 The second quantitative kit (Method C) involves a titration of the extracted sample with mercuric nitrate by means of a 1-mL microburette such that the end point is denoted by a change from pale yellow to red-violet over the range of the kit (300 to 4,000 μg/g). The concentration of chlorine in the original oil is then read from a scale on the microburette.

NOTE: Warning--All reagents are encapsulated or contained within ampoules. Strict adherence to the operational procedures included with the kits as well as accepted safety procedures (safety glasses and gloves) should be observed.

NOTE: Warning--When crushing the glass ampoules, press firmly in the center of the ampoule once. Never attempt to recrush broken glass because the glass may come through the plastic and cut fingers.

NOTE: Warning--In case of accidental breakage onto skin or clothing, wash with large amounts of water. All the ampoules are poisonous and should not be taken internally.

NOTE: Warning--The gray ampoules contain metallic sodium. Metallic sodium is a flammable water-reactive solid.

NOTE: Warning--Do not ship kits on passenger aircraft. Dispose of used kits properly.

NOTE: Caution--When the sodium ampoule in either kit is crushed, oils that contain more than 25% water will cause the sample to turn clear to light gray. Under these circumstances, the results may be biased excessively low and should be disregarded.

3.0 INTERFERENCES

3.1 Free water, as a second phase, should be removed. However, this second phase can be analyzed separately for chloride content if desired.

METHOD A

FIXED END POINT TEST KIT METHOD

4.0A APPARATUS AND MATERIALS

4.1A The CLOR-D-TECT 1000[1] is a complete self-contained kit. It includes: a sampling tube to withdraw a fixed sample volume for analysis; a polyethylene test tube #1 into which the sample is introduced for dilution and reaction with metallic sodium; and a polyethylene tube #2 containing a buffered aqueous extractant, the mercuric nitrate titrant, and diphenyl carbazone indicator. Included are instructions to conduct the test and a color chart to aid in determining the end point.

5.0A REAGENTS

5.1A Purity of reagents. Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2A All necessary reagents are contained within the kit.

5.3A The kit should be examined upon opening to see that all of the components are present and that all the ampoules (4) are in place and not leaking. The liquid in Tube #2 (yellow cap) should be approximately 1/2 in. above the 5-mL line and the tube should not be leaking. The ampoules are not supposed to be completely full.

6.0A SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1A All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2A Because the collected sample will be analyzed for total halogens, it should be kept headspace free and refrigerated prior to preparation and analysis to minimize volatilization losses of organic halogens. Because waste oils may contain toxic and/or carcinogenic substances, appropriate field and laboratory safety procedures should be followed.

7.0A PROCEDURE

7.1A Preparation. Open analysis carton, remove contents, mount plastic test tubes in the provided holder. Remove syringe and glass sampling capillary from foil pouch.

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[1]Available from Dexsil Corporation, One Hamden Park Drive, Hamden, CT 06517.

NOTE: Perform the test in a warm, dry area with adequate light. In cold weather, a truck cab is sufficient. If a warm area is not available, Step 7.3A should be performed while warming Tube #1 in palm of hand.

7.2A Sample introduction. Remove white cap from Tube #1. Using the plastic syringe, slowly draw the oil up the capillary tube until it reaches the flexible adapter tube. Wipe excess oil from the tube with the provided tissue, keeping capillary vertical. Position capillary tube into Tube #1, and detach adapter tubing, allowing capillary to drop to the bottom of the tube. Replace white cap on tube. Crush the capillary by squeezing the test tube several times, being careful not to break the glass reagent ampoules.

7.3A Reaction. Break the lower (colorless) capsule containing the clear diluent solvent by squeezing the sides of the test tube. Mix thoroughly by shaking the tube vigorously for 30 seconds. Crush the upper grey ampoule containing metallic sodium, again by squeezing the sides of the test tube. Shake vigorously for 20 seconds. Allow reaction to proceed for 60 seconds, shaking intermittently several times while timing with a watch.

NOTE: Caution--Always crush the clear ampoule in each tube first. Otherwise, stop the test and start over using another complete kit. False (low) results may occur and allow a contaminated sample to pass without detection if clear ampoule is not crushed first.

7.4A Extraction. Remove caps from both tubes. Pour the clear buffered extraction solution from Tube #2 into Tube #1. Replace the white cap on Tube #1, and shake vigorously for 10 seconds. Vent tube by partially unscrewing the dispenser cap. Close cap securely, and shake for an additional 10 seconds. Vent again, tighten cap, and stand tube upside down on white cap. Allow phases to separate for 2 minutes.

7.5A Analysis. Put filtration funnel into Tube #2. Position Tube #1 over funnel and open nozzle on dispenser cap. Squeeze the sides of Tube #1 to dispense the clear aqueous lower phase through the filter into Tube #2 to the 5 mL line on Tube #2. Remove the filter funnel. Replace the yellow cap on Tube #2 and close the nozzle on the dispenser cap. Break the colorless lower capsule containing mercuric nitrate solution by squeezing the sides of the tube, and shake for 10 seconds. Then break the upper colored ampoule containing the diphenylcarbazone indicator, and shake for 10 seconds. Observe color immediately.

7.6A Interpretation of results

7.6.1A Because all reagent levels are preset, calculations are not required. A blue solution in Tube #2 indicates a chlorine content in the original oil of less than 1,000 μg/g, and a yellow color indicates that the chlorine concentration is greater than 1,000 μg/g. Refer to the color chart enclosed with the kit in interpreting the titration end point.

7.6.2A Report the results as < or > 1,000 μg/g chlorine in the oil sample.

8.0A QUALITY CONTROL

8.1A Refer to Chapter One for specific quality control procedures.

8.2A Each sample should be tested two times. If the results do not agree, then a third test must be performed. Report the results of the two that agree.

9.0A METHOD PERFORMANCE

9.1A No formal statement is made about either the precision or bias of the overall test kit method for determining chlorine in used oil because the result merely states whether there is conformance to the criteria for success specified in the procedure, (i.e., a blue or yellow color in the final solution). In a collaborative study, eight laboratories analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate using the test kit. Of the resulting 56 data points, 3 resulted in incorrect classification of the oil's chlorine content (Table 1). A data point represents one duplicate analysis of a sample. There were no disagreements within a laboratory on any duplicate determinations.

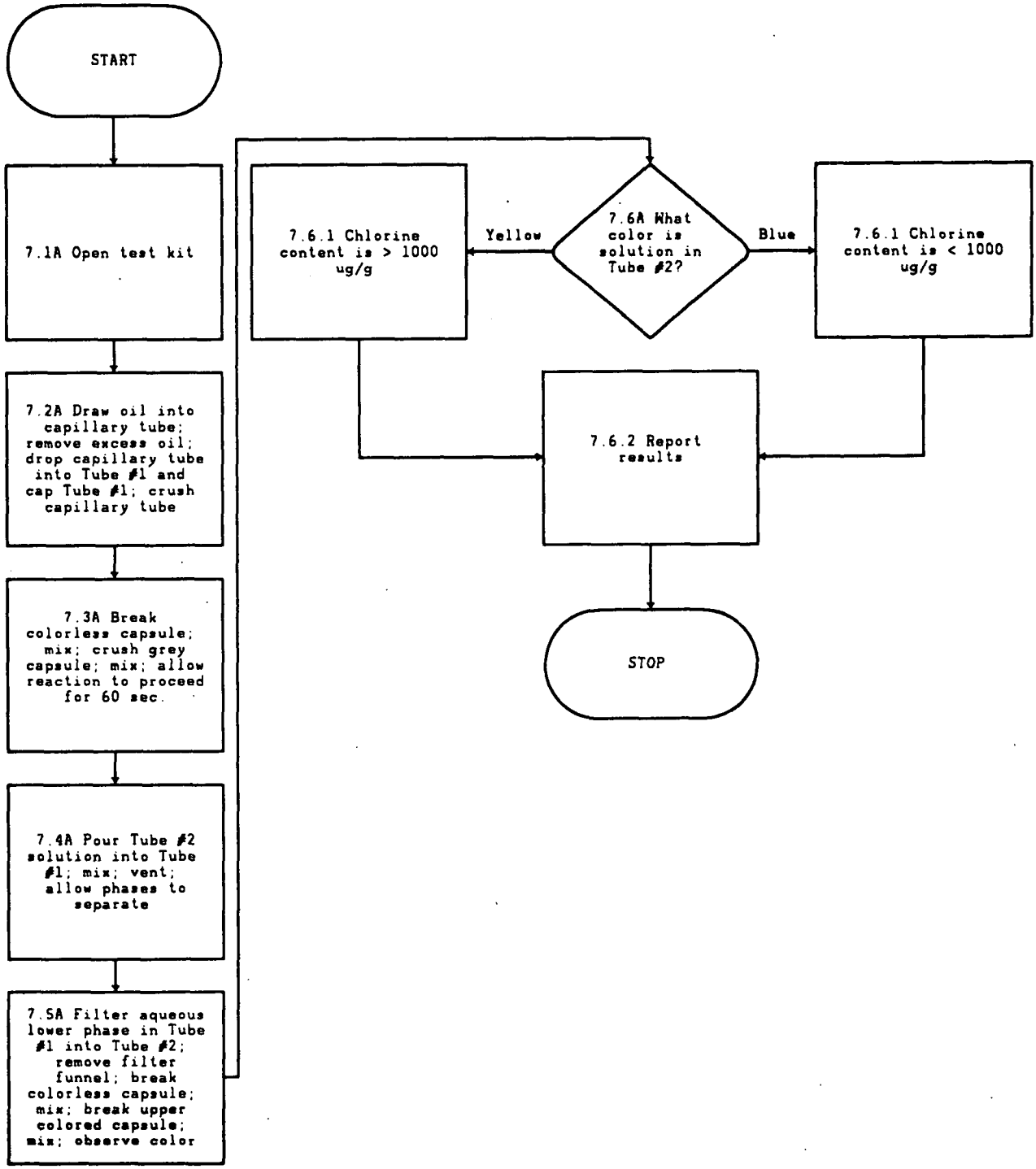
TABLE 1.
PRECISION AND BIAS INFORMATION FOR METHOD A-
FIXED END POINT TEST KIT METHOD

Expected concentration, µg/g	Expected results, µg/g	Percent correct[a]	Percent agreement[b]	
			Within	Between
320	< 1,000	100	100	100
480	< 1,000	100	100	100
920	< 1,000	100	100	100
1,498	> 1,000	87	100	87
1,527	> 1,000	75	100	75
3,029	> 1,000	100	100	100
3,045	> 1,000	100	100	100

[a]Percent correct--percent correctly identified as above or below 1,000 µg/g.

[b]Percent agreement--percent agreement within or between laboratories.

METHOD 9077, METHOD A
FIXED END POINT TEST KIT METHOD



METHOD B

REVERSE TITRATION QUANTITATIVE END POINT TEST KIT METHOD

4.0B APPARATUS AND MATERIALS

4.1B QuantiClor[2] kit components (see Figure 1).

4.1.1B Plastic reaction bottle: 1 oz, with flip-top dropper cap and a crushable glass ampoule containing sodium.

4.1.2B Plastic buffer bottle: contains 9.5 mL of aqueous buffer solution.

4.1.3B Titration vial: contains buffer bottle and indicator-impregnated paper.

4.1.4B Glass vial: contains 2.0 mL of solvents.

4.1.5B Micropipet and plunger, 0.25 mL.

4.1.6B Activated carbon filtering column.

4.1.7B Titret and valve assembly.

4.2B The reagents needed for the test are packaged in disposable containers.

4.3B The procedure utilizes a Titret. Titrets® are hand-held, disposable cells for titrimetric analysis. A Titret is an evacuated glass ampoule (13 mm diameter) that contains an exact amount of a standardized liquid titrant. A flexible valve assembly is attached to the tip of the ampoule. Titrets® employ the principle of reverse titration; that is, small doses of sample are added to the titrant to the appearance of the end point color. The color change indicates that the equivalency point has been reached. The flow of the sample into the Titret may be controlled by using an accessory called a Titrettor™ .

5.0B REAGENTS

5.1B The crushable glass ampoule, which is inside the reaction bottle, contains 85 mg of metallic sodium in a light oil dispersion.

5.2B The buffer bottle contains 0.44 g of $NaH_2PO_4 \cdot 2H_2O$ and 0.32 mL of HNO_3 in distilled water.

5.3B The glass vial contains 770 mg Stoddard Solvent (CAS No. 8052-41-3), 260 mg toluene, 260 mg butyl ether, 260 mg diglyme, 130 mg naphthalene, and 70 mg demulsifier.

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[2]Quanti-Chlor Kit, Titrets®, and Titrettor™ are manufactured by Chemetrics, Inc., Calverton, VA 22016. U.S. Patent No. 4,332,769.

5.4B The Titret contains 1.12 mg mercuric nitrate in distilled water.

5.5B The indicator-impregnated paper contains approximately 0.3 mg of diphenylcarbazone and 0.2 mg of brilliant yellow.

6.0B SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See Section 6.0A of Method A.

7.0B PROCEDURE

7.1B Shake the glass vial and pour its contents into the reaction bottle.

7.2B Fill the micropipet with a well-shaken oil sample by pulling the plunger until its top edge is even with the top edge of the micropipet. Wipe off the excess oil and transfer the sample into the reaction bottle (see Figure 2.1).

7.3B Gently squeeze most of the air out of the reaction bottle (see Figure 2.2). Cap the bottle securely, and shake vigorously for 30 seconds.

7.4B Crush the sodium ampoule by pressing against the outside wall of the reaction bottle (see Figure 2.3).

> CAUTION: Samples containing a high percentage of water will generate heat and gas, causing the reaction bottle walls to expand. To release the gas, briefly loosen the cap.

7.5B Shake the reaction bottle vigorously for 30 seconds.

7.6B Wait 1 minute. Shake the reaction bottle occasionally during this time.

7.7B Remove the buffer bottle from the titration vial, and slowly pour its contents into the reaction bottle (see Figure 2.4).

7.8B Cap the reaction bottle and shake gently for a few seconds. As soon as the foam subsides, release the gas by loosening the cap. Tighten the cap, and shake vigorously for 30 seconds. As before, release any gas that has formed, then turn the reaction bottle upside down (see Figure 2.5).

7.9B Wait 1 minute.

7.10B While holding the filtering column in a vertical position, remove the plug. Gently tap the column to settle the carbon particles.

7.11B Keeping the reaction bottle upside down, insert the flip top into the end of the filtering column and position the column over the titration vial (see Figure 2.6). Slowly squeeze the lower aqueous layer out of the reaction bottle and into the filtering column. Keep squeezing until the first drop of oil is squeezed out.

NOTE: Caution--The aqueous layer should flow through the filtering column into the titration vial in about 1 minute. In rare cases, it may be necessary to gently tap the column to begin the flow. The indicator paper should remain in the titration vial.

7.12B Cap the titration vial and shake it vigorously for 10 seconds.

7.13B Slide the flexible end of the valve assembly over the tapered tip of the Titret so that it fits snugly (see Figure 3.1).

7.14B Lift (see Figure 3.2) the control bar and insert the assembled Titret into the Titrettor™ .

7.15B Hold the Titrettor™ with the sample pipe in the sample, and press the control bar to snap the pre-scored tip of the Titret (see Figure 3.3).

NOTE: Caution--Because the Titret is sealed under vacuum, the fluid inside may be agitated when the tip snaps.

7.16B With the tip of the sample pipe in the sample, briefly press the control bar to pull in a SMALL amount of sample (see Figure 3.3). The contents of the Titret will turn purple.

CAUTION: During the titration, there will be some undissolved powder inside the Titret. This does not interfere with the accuracy of the test.

7.17B Wait 30 seconds.

7.18B Gently press the control bar again to allow another SMALL amount of the sample to be drawn into the Titret.

CAUTION: Do not press the control bar unless the sample pipe is immersed in the sample. This prevents air from being drawn into the Titret.

7.19B After each addition, rock the entire assembly to mix the contents of the Titret. Watch for a color change from purple to very pale yellow.

7.20B Repeat Steps 7.18B and 7.19B until the color change occurs.

CAUTION: The end point color change (from purple to pale yellow) actually goes through an intermediate gray color. During this intermediate stage, extra caution should be taken to bring in SMALL amounts of sample and to mix the Titret contents well.

7.21B When the color of the liquid in the Titret changes to PALE YELLOW, remove the Titret from the Titrettor™ . Hold the Titret in a vertical position and carefully read the test result on the scale opposite the liquid level.

7.22B Calculation

7.22.1B To obtain results in micrograms per gram total chlorine, multiply scale units on the Titret by 1.3 and then subtract 200.

8.0B QUALITY CONTROL

8.1B Refer to Chapter One for specific quality control procedures.

8.2B Each sample should be tested two times. If the results do not agree to within 10%, expressed as the relative percent difference of the results, a third test must be performed. Report the results of the two that agree.

9.0B METHOD PERFORMANCE

9.1B These data are based on 49 data points obtained by seven laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. A data point represents one duplicate analysis of a sample. There were no outlier data points or laboratories.

9.2B Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 2):

$$Repeatability = 0.31\ x*$$

*where x is the average of two results in μg/g.

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$Reproducibility = 0.60\ x*$$

*where x is the average value of two results in μg/g.

9.3B Bias. The bias of this test method varies with concentration, as shown in Table 3:

Bias = Amount found - Amount expected

TABLE 2.
REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED OILS BY THE QUANTITATIVE END POINT TEST KIT METHOD

Average value, µg/g	Repeatability, µg/g	Reproducibility, µg/g
1,000	310	600
1,500	465	900
2,000	620	1,200
2,500	775	1,500
3,000	930	1,800

TABLE 3.
RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY THE QUANTITATIVE END POINT TEST KIT METHOD

Amount expected, µg/g	Amount found, µg/g	Bias, µg/g	Percent bias
320 (< 750)[a]	776	+16	+3
480 (< 750)[a]	782	+32	+4
920	1,020	+100	+11
1,498	1,129	-369	-25
1,527	1,434	-93	-6
3,029	1,853	-1,176	-39
3,045	2,380	-665	-22

[a] The lower limit of the kit is 750 µg/g.

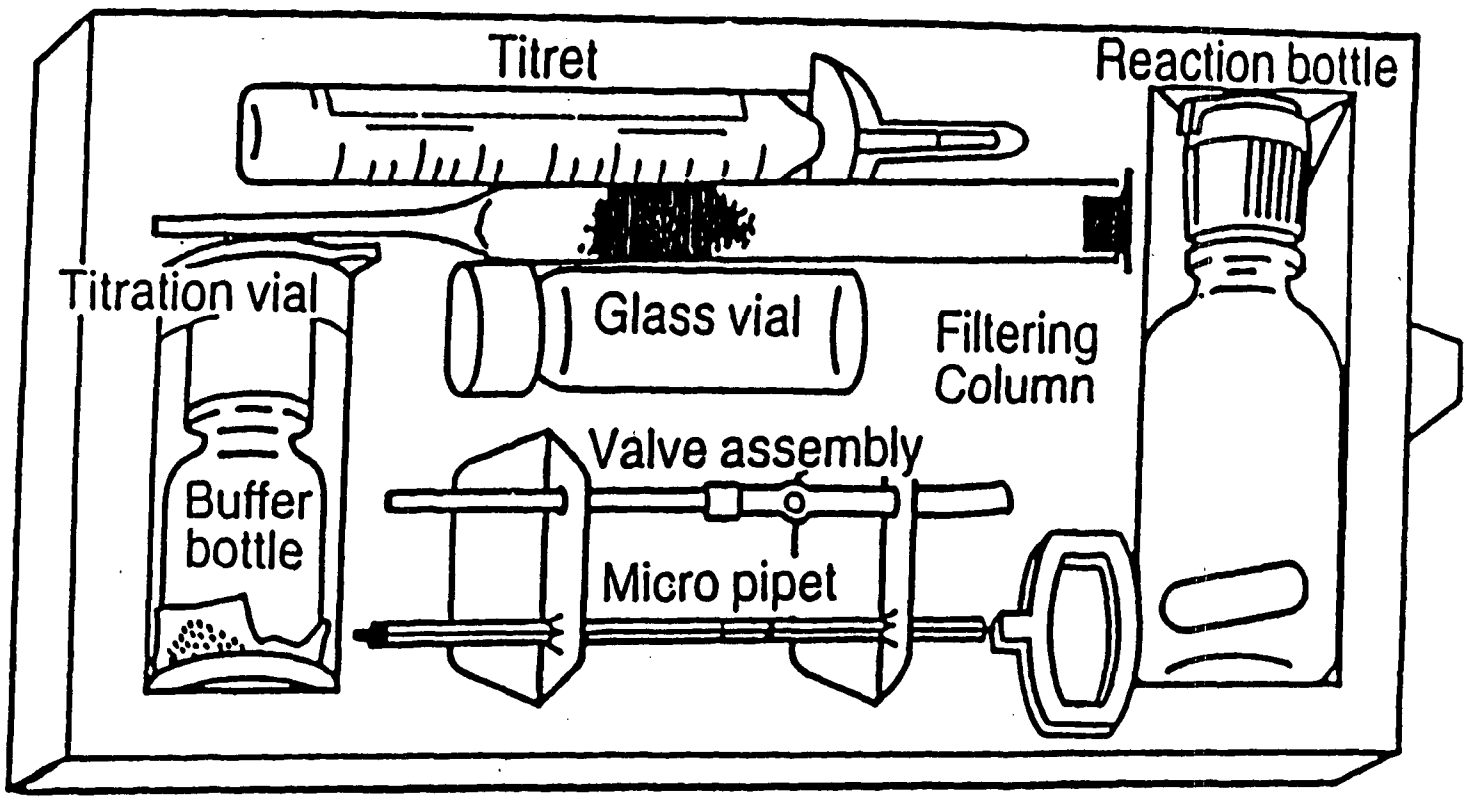


Figure 1. Components of CHEMetrics Total Chlorine in Waste Oil Test Kit (Cat. No. K2610).

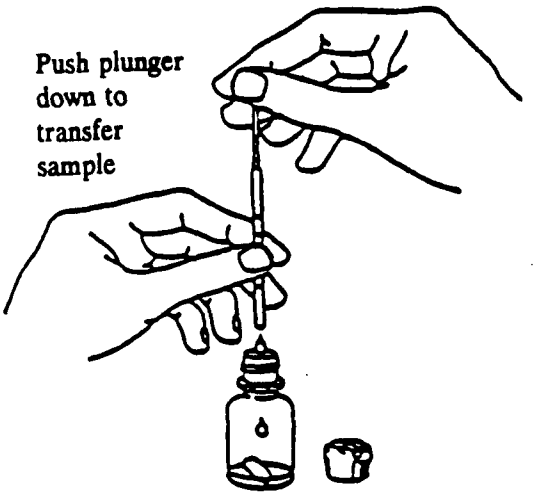


Figure 2.1

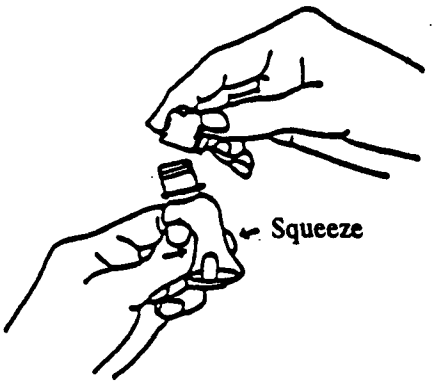


Figure 2.2

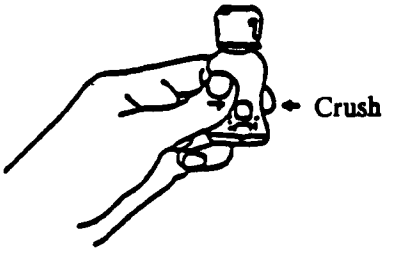


Figure 2.3

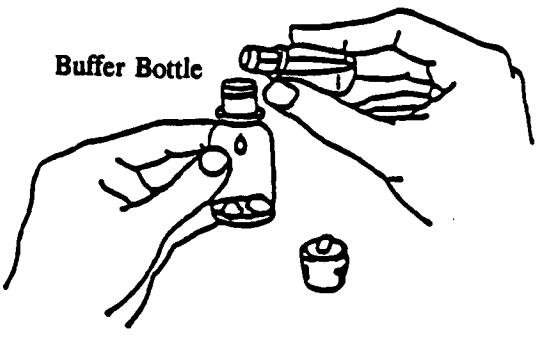


Figure 2.4

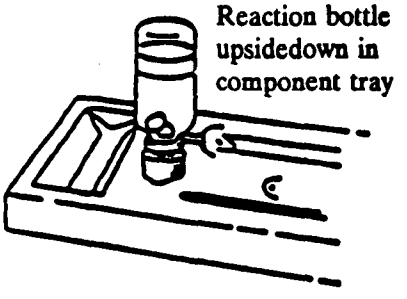


Figure 2.5

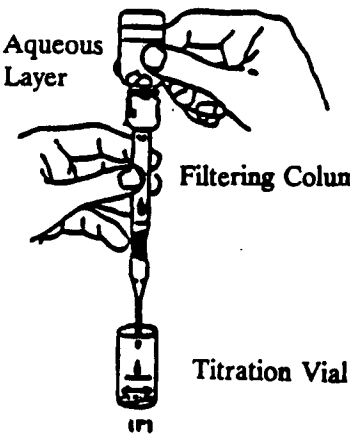
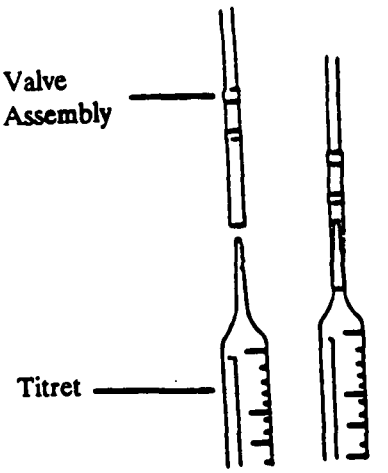


Figure 2.6

Figure 2. Reaction-Extraction Procedure.

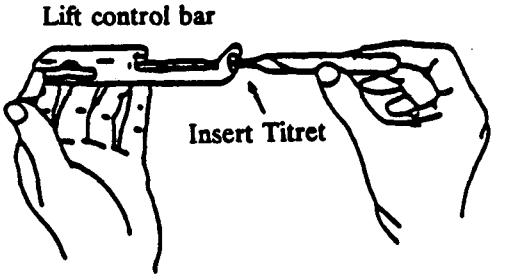
Attaching the Valve Assembly

Figure 3.1



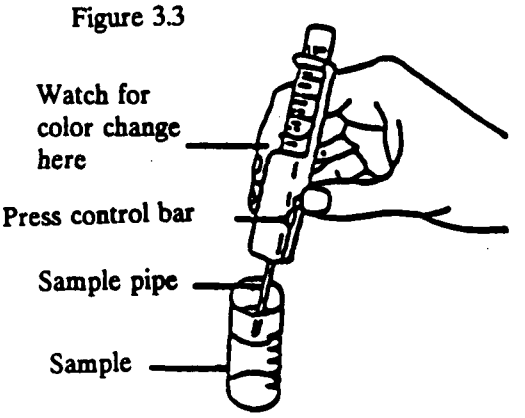
Snapping the Tip

Figure 3.2



Performing the Analysis

Figure 3.3

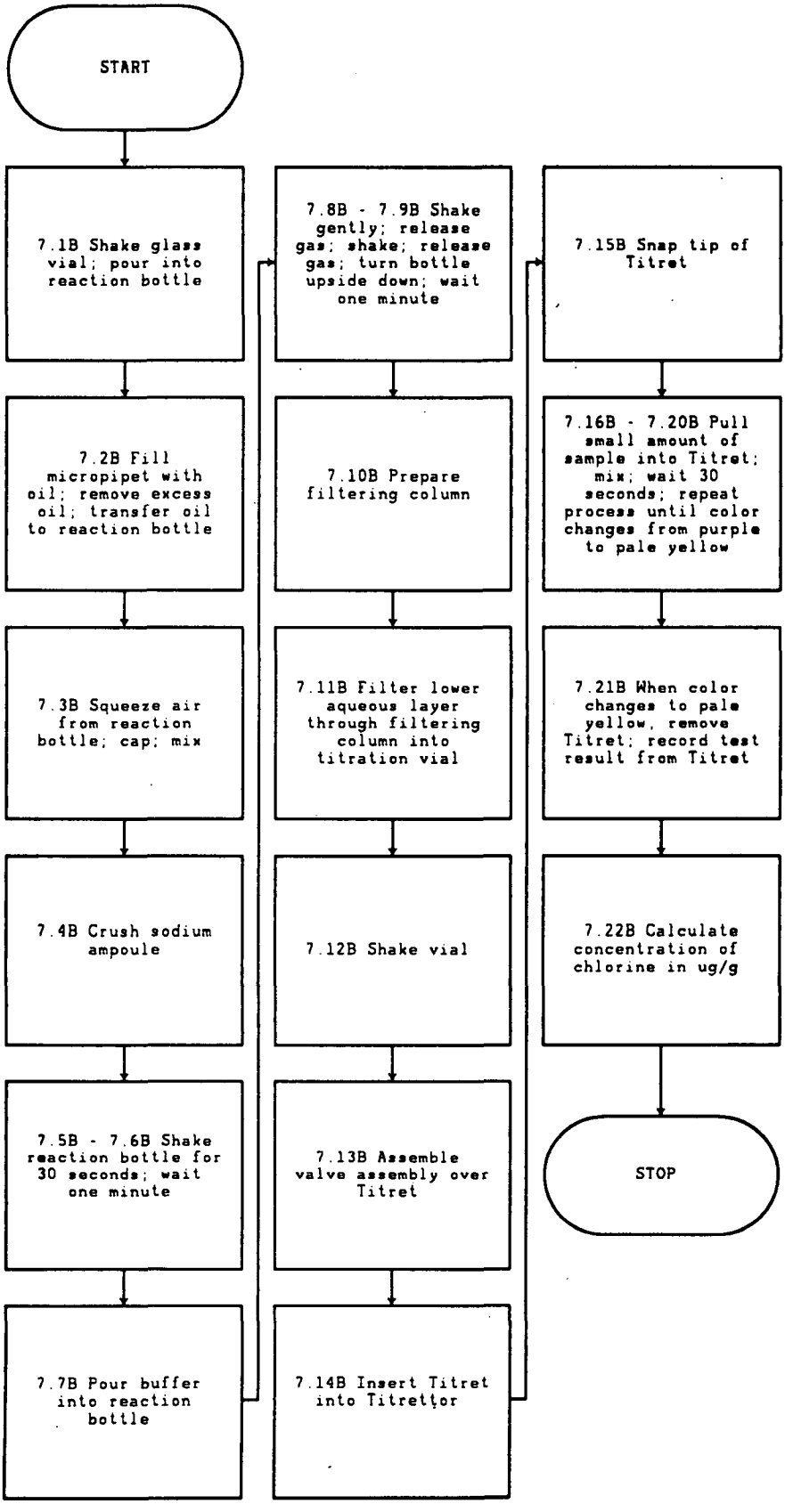


Reading the Result

Figure 3.4

Figure 3. Titration Procedure

METHOD 9077, METHOD B
REVERSE TITRATION QUANTITATIVE END POINT TEST KIT METHOD



METHOD C

DIRECT TITRATION QUANTITAVE END POINT TEST KIT METHOD

4.0C APPARATUS AND MATERIALS

4.1C The CHLOR-D-TECT Q4000[3] is a complete self-contained kit. It includes: a sampling syringe to withdraw a fixed sample volume for analysis; a polyethylene test tube #1 into which the sample is introduced for dilution and reaction with metallic sodium; a polyethylene tube #2 containing a buffered aqueous extractant and the diphenylcarbazone indicator; a microburette containing the mercuric nitrate titrant; and a plastic filtration funnel. Also included are instructions to conduct the test.

5.0C REAGENTS

5.1C All necessary reagents are contained within the kit. The diluent solvent containing the catalyst, the metallic sodium, and the diphenylcarbazone are separately glass-encapsulated in the precise quantity required for analysis. A predispensed volume of buffer is contained in the second polyethylene tube. Mercuric nitrate titrant is also supplied in a sealed titration burette.

5.2C The kit should be examined upon opening to see that all of the components are present and that all ampoules (3) are in place and not leaking. The liquid in Tube #2 (clear cap) should be approximately 1/2 in. above the 5-mL line and the tube should not be leaking. The ampoules are not supposed to be completely full.

6.0C SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1C See Section 6.0A of Method A.

7.0C PROCEDURE

7.1C Preparation. Open analysis carton, remove contents, mount plastic test tubes in the provided holder.

> NOTE: Perform the test in a warm, dry area with adequate light. In cold weather, a truck cab is sufficient. If a warm area is not available, Step 7.3C should be performed while warming Tube #1 in palm of hand.

7.2C Sample introduction. Unscrew the white dispenser cap from Tube #1. Slide the plunger in the empty syringe a few times to make certain that it slides easily. Place the top of the syringe in the oil sample to be tested, and pull back on the plunger until it reaches the stop and cannot be pulled further. Remove the syringe from the sample container, and wipe any excess oil from the outside of the syringe with the enclosed tissue. Place the tip of the syringe in Tube #1, and dispense the oil sample by depressing the plunger. Replace the white cap on the tube.

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[3]Available from Dexsil Corporation, One Hamden Park Drive, Hamden, CT 06517.

7.3C Reaction. Break the lower (colorless) capsule containing the clear diluent solvent by squeezing the sides of the test tube. Mix thoroughly by shaking the tube vigorously for 30 seconds. Crush the upper grey ampoule containing metallic sodium, again by squeezing the sides of the test tube. Shake vigorously for 20 seconds. Allow reaction to proceed for 60 seconds, shaking intermittently several times while timing with a watch.

> CAUTION: Always crush the clear ampoule in each tube first. Otherwise, stop the test and start over using another complete kit. False (low) results may occur and allow a contaminated sample to pass without detection if clear ampoule is not crushed first.

7.4C Extraction. Remove caps from both tubes. Pour the clear buffered extraction solution from Tube #2 into Tube #1. Replace the white cap on Tube #1, and shake vigorously for 10 seconds. Vent tube by partially unscrewing the dispenser cap. Close cap securely, and shake for an additional 10 seconds. Vent again, tighten cap, and stand tube upside down on white cap. Allow phases to separate for 2 minutes.

> NOTE: Tip Tube #2 to an angle of only about 45°. This will prevent the holder from sliding out.

7.5C Analysis. Put filtration funnel into Tube #2. Position Tube #1 over funnel and open nozzle on dispenser cap. Squeeze the sides of Tube #1 to dispense the clear aqueous lower phase through the filter into Tube #2 to the 5-mL line on Tube #2. Remove the filter funnel, and close the nozzle on the dispenser cap. Place the plunger rod in the titration burette and press until it clicks into place. Break off (do not pull off) the tip on the titration burette. Insert the burette into Tube #2, and tighten the cap. Break the colored ampoule, and shake gently for 10 seconds. Dispense titrant dropwise by pushing down on burette rod in small increments. Shake the tube gently to mix titrant with solution in Tube #2 after each increment. Continue adding titrant until solution turns from yellow to red-violet. An intermediate pink color may develop in the solution, but should be disregarded. Continue titrating until a true red-violet color is realized. The chlorine concentration of the original oil sample is read directly off the titrating burette at the tip of the black plunger. Record this result immediatley as the red-violet color will fade with time.

8.0C QUALITY CONTROL

8.1C Refer to Chapter One for specific quality control procedures.

8.2C Each sample should be tested two times. If the results do not agree to within 10%, expressed as the relative percent difference of the results, a third test must be performed. Report the results of the two that agree.

9.0C METHOD PERFORMANCE

9.1C These data are based on 96 data points obtained by 12 laboratories who each analyzed six used crankcase oils and two fuel oil blends with crankcase in duplicate. A data point represents one duplicate analysis of a sample.

9.2C Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 4):

$$Repeatability = 0.175\ x*$$

*where x is the average of two results in µg/g.

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$Reproducibility = 0.331\ x*$$

*where x is the average value of two results in µg/g.

9.3C Bias. The bias of this test method varies with concentration, as shown in Table 5:

Bias = Amount found - Amount expected

10.0 REFERENCE

1. Gaskill, A.; Estes, E.D.; Hardison, D.L.; and Myers, L.E. Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels. Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, wA 80. July 1988.

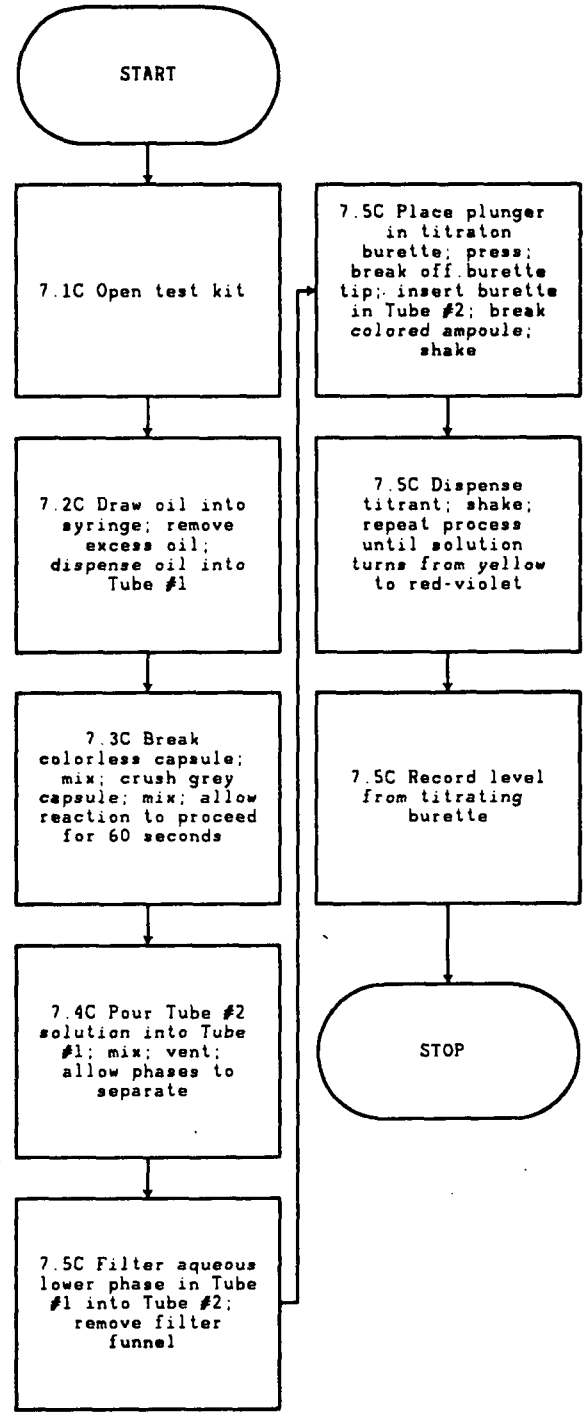
TABLE 4.
REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED OILS BY THE QUANTITATIVE END POINT TEST KIT METHOD

Average value, µg/g	Repeatability, µg/g	Reproducibility, µg/g
500	88	166
1,000	175	331
1,500	263	497
2,000	350	662
2,500	438	828
3,000	525	993
4,000	700	1,324

TABLE 5.
RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY THE QUANTITATIVE END POINT TEST KIT METHOD

Amount expected, µg/g	Amount found, µg/g	Bias, µg/g	Percent bias
664	695	31	+5
964	906	-58	-6
1,230	1,116	-114	-9
1,445	1,255	-190	-13
2,014	1,618	-396	-20
2,913	2,119	-794	-27
3,812	2,776	-1,036	-27
4,190	3,211	-979	-23

METHOD 9077, METHOD C
DIRECT TITRATION QUANTITAVE END POINT TEST KIT METHOD



METHOD 9131

TOTAL COLIFORM: MULTIPLE TUBE FERMENTATION TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the presence of a member of the coliform group in ground water and surface water.

1.2 The coliform group, as analyzed for in this procedure, is defined as all aerobic and facultative anaerobic, gram-negative, non-spore-forming, rod-shaped bacteria that ferment lactose with gas formation within 48 hr at 35°C.

2.0 SUMMARY OF METHOD

2.1 The multiple-tube fermentation technique is a three-stage procedure in which the results are statistically expressed in terms of the Most Probable Number (MPN). These stages -- the presumptive stage, confirmed stage, and completed test -- are briefly summarized below. (For the analysis to be accurate, a five-tube test is required.)

2.1.1 **Presumptive Stage:** A series of lauryl tryptose broth primary fermentation tubes are inoculated with graduated quantities of the sample to be tested. The inoculated tubes are incubated at 35 ± 0.5°C for 24 ± 2 hr, at which time the tubes are examined for gas formation. For the tubes in which no gas is formed, continue incubation and examine for gas formation at the end of 48 ± 3 hr. Formation of gas in any amount within 48 ± 3 hr is a positive presumptive test.

2.1.2 **Confirmed Stage:** The confirmed stage is used on all primary fermentation tubes showing gas formation during the 24-hr and 48-hr periods. Fermentation tubes containing brilliant green lactose bile broth are inoculated with medium from the tubes showing a positive result in the presumptive test. Inoculation should be performed as soon as possible after gas formation occurs. The inoculated tubes are incubated for 48 ± 3 hr at 35 ± 0.5°C. Formation of gas at any time in the tube indicates a positive confirmed test.

2.1.3 **Completed Test:** The completed test is performed on all samples showing a positive result in the confirmed test. It can also be used as a quality control measure on 20% of all samples analyzed. One or more plates of eosin methylene blue are streaked with sample to be analyzed. The streaked plates are incubated for 24 ± 2 hr at 35 ± 0.5°C. After incubation, transfer one or more typical colonies (nucleated, with or without metallic sheen) to a lauryl tryptose broth fermentation tube and a nutrient agar slant. The fermentation tubes and agar slants are incubated at 35 ± 0.5°C for 24 ± 2 hr, or for 48 ± 3 hr if gas is not produced. From the agar slants corresponding to the fermentation tubes in which gas formation occurs, gram-stained samples are examined

microscopically. The formation of gas in the fermentation tube and the presence of gram-negative, non-spore-forming, rod-shaped bacteria in the agar culture may be considered a satisfactorily completed test, demonstrating the positive presence of coliform bacteria in the analyzed sample.

2.2 More detailed treatment of this method is presented in Standard Methods for the Examination of Water and Wastewater and in Microbiological Methods for Monitoring the Environment (see References, Section 10.0).

3.0 INTERFERENCES

3.1 The distribution of bacteria in water is irregular. Thus, a five-tube test is required in this method for adequate statistical accuracy.

3.2 The presence of residual chlorine or other halogens can prevent the continuation of bacterial action. To prevent this occurrence, sodium thiosulfate should be added to the sterile sample container.

3.3 Water samples high in copper, zinc, or other heavy metals can be toxic to bacteria. Chelating agents such as ethylenediaminetetraacetic acid (EDTA) should be added only when heavy metals are suspected of being present.

3.4 It is important to keep in mind that MPN tables are probability calculations and inherently have poor precision. They include a 23% positive bias that generally results in high value. The precision of the MPN can be improved by increasing the number of sample portions examined and the number of samples analyzed from the same sampling point.

4.0 APPARATUS AND MATERIALS

4.1 Incubators:

4.1.1 Incubators must maintain a uniform and constant temperature at all times in all areas, that is, they must not vary more than ± 0.5°C in the areas used. Obtain such accuracy by using a water-jacketed or anhydric-type incubator with thermostatically controlled low-temperature electric heating units properly insulated and located in or adjacent to the walls or floor of the chamber and preferably equipped with mechanical means of circulating air. If a hot-air type incubator is used, humidity must be maintained at 75-80%.

4.1.2 Alternatively, use special incubating rooms well insulated and equipped with properly distributed heating units and with forced air circulation, provided that they conform to desired temperature limits and relative humidity. When such rooms are used, record the daily temperature range in areas where plates or tubes are incubated. Provide incubators with open metal wire or sheet shelves so spaced as to assure temperature uniformity throughout the chamber. Leave a 2.5-cm space between walls and stacks of dishes or baskets of tubes.

4.1.3 Maintain an accurate thermometer with the bulb immersed in liquid (glycerine, water, or mineral oil) on each shelf in use within the incubator and record daily temperature readings (preferably morning and afternoon). It is desirable, in addition, to maintain a maximum and minimum registering thermometer within the incubator on the middle shelf to record the gross temperature range over a 24-hr period. At intervals, determine temperature variations within the incubator when filled to maximum capacity. Install a recording thermometer, whenever possible, to maintain a continuous and permanent record of temperature. Mercury thermometers should be graduated in 0.5°C increments and calibrated annually against an NBS certified thermometer. Dial thermometers should be calibrated quarterly.

4.1.4 Keep water depth in the water bath sufficient to immerse tubes to upper level of media.

4.2 Hot-air sterilizing ovens: Use hot-air sterilizing ovens of sufficient size to prevent internal crowding, constructed to give uniform and adequate sterilizing temperatures of 170 ± 10°C and equipped with suitable thermometers. As an alternative, use a temperature-recording instrument.

4.3 Autoclaves:

4.3.1 Use autoclaves of sufficient size to prevent internal crowding, constructed to provide uniform temperatures within the chambers (up to and including the sterilization temperature of 121°C); equipped with an accurate thermometer, the bulb of which is located properly on the exhaust line so as to register minimum temperature within the sterilizing chambers (temperature-recording instrument is optional); equipped with pressure gauge and properly adjusted safety valves connected directly with saturated-steam power lines or directly to a suitable special steam generator (do not use steam from a boiler treated with amines for corrosion control); and capable of reaching the desired temperature within 30 min.

4.3.2 Use of a vertical autoclave or pressure cooker is not recommended because of difficulty in adjusting and maintaining sterilization temperature and the potential hazard. If a pressure cooker is used in emergency or special circumstances, equip it with an efficient pressure gauge and a thermometer, the bulb of which is 2.5 cm above the water level.

4.4 Colony counters: Use Quebec-type colony counter, dark-field model preferred, or one providing equivalent magnification (1.5 diameters) and satisfactory visibility.

4.5 pH Equipment: Use electrometric pH meters, accurate to at least 0.1 pH units, for determining pH values of media. See Method 9040 for standardization of a pH meter.

4.6 Balances: Use balances providing a sensitivity of at least 0.1 g at a load of 150 g, with appropriate weights. Use an analytical balance having a sensitivity of 1 mg under a load of 10 g for weighing small quantities (less than 2 g) of materials. Single-pan rapid-weigh balances are most convenient.

4.7 Media preparation utensils: Use borosilicate glass or other suitable noncorrosive equipment such as stainless steel. Use glassware that is clean and free of residues, dried agar, or other foreign materials that may contaminate media.

4.8 Pipets and graduated cylinders:

4.8.1 Use pipets of any convenient size, provided that they deliver the required volume accurately and quickly. The error of calibration for a given manufacturer's lot must not exceed 2.5%. Use pipets having graduations distinctly marked and with unbroken tips. Bacteriological-transfer pipets or pipets conforming to the APHA standards given in the latest edition of Standard Methods for the Examination of Dairy Products may be used. Optimally, protect the mouth end of all pipets by a cotton plug to eliminate hazards to the worker or possible sample contamination by saliva.

4.8.2 Use graduated cylinders meeting ASTM Standards (D-86 and D-216) and with accuracy limits established by the National Bureau of Standards, where appropriate.

4.9 Pipet containers: Use boxes of aluminum or stainless steel, end measurement 5 to 7.5 cm, cylindrical or rectangular, and length about 40 cm. When these are not available, paper wrappings may be substituted. To avoid excessive charring during sterilization, use best-quality sulfate pulp (Kraft) paper. Do not use copper or copper alloy cans or boxes as pipet containers.

4.10 Dilution bottles or tubes:

4.10.1 Use bottles or tubes of resistant glass, preferably borosilicate glass, closed with glass stoppers or screw caps equipped with liners that do not produce toxic or bacteriostatic compounds on sterilization.

4.10.2 Do not use cotton plugs as closures. Mark gradation levels indelibly on side of dilution bottle or tube. Plastic bottles of nontoxic material and acceptable size may be substituted for glass, provided that they can be sterilized properly.

4.11 Petri dishes: Use glass or plastic Petri dishes about 100 x 15 mm. Use dishes the bottoms of which are free from bubbles and scratches and flat so that the medium will be of uniform thickness throughout the plate. For the membrane-filter technique, use loose-lid glass or plastic dishes, 60 x 15 mm, or tight-lid dishes, 50 x 12 mm. Sterilize Petri dishes and store in metal cans (aluminum or stainless steel, but not copper), or wrap in paper -- preferably best-quality sulfate pulp (Kraft) -- before sterilizing.

4.12 Fermentation tubes and vials: Use only 10-mm x 75-mm fermentation tubes. When tubes are used for a test of gas production, enclose a shell vial, inverted. Use a vial of such size that it will be filled completely with medium and at least partly submerged in the tube.

4.13 Inoculating equipment: Use wire loops made of 22- or 24-gauge nickel alloy (chromel, nichrome, or equivalent) or platinum-iridium for flame sterilization. Single-service transfer loops of aluminum or stainless steel are satisfactory. Use loops at least 3 mm in diameter. Sterilize by dry heat or steam. Single-service hardwood applicators also may be used. Make these 0.2 to 0.3 cm in diameter and at least 2.5 cm longer than the fermentation tube; sterilize by dry heat and store in glass or other nontoxic containers.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Buffered water:

5.2.1 To prepare stock phosphate buffer solution, dissolve 34.0 g potassium dihydrogen phosphate (KH_2PO_4) in 500 mL Type II water, adjust to pH 7.2 ± 0.5 with 1 N sodium hydroxide (NaOH), and dilute to 1 liter with Type II water.

5.2.2 Add 1.25 mL stock phosphate buffer solution and 5.0 mL magnesium chloride solution (38 g $MgCl_2$/liter Type II water or 81.1 g $MgCl_2 \cdot 6H_2O$/liter Type II water) to 1 liter Type II water. Dispense in amounts that will provide 99 ± 2.0 mL or 9 ± 0.2 mL after autoclaving for 15 min.

5.2.3 Peptone water: Prepare a 10% solution of peptone in Type II water. Dilute a measured volume to provide a final 0.1% solution. Final pH should be 6.8.

5.2.4 Dispense in amounts to provide 99 ± 2.0 mL or 9 ± 0.2 mL after autoclaving for 15 min.

5.2.5 Do not suspend bacteria in any dilution water for more than 30 min at room temperature because death or multiplication may occur, depending on the species.

5.3 Lauryl tryptose broth:

5.3.1 Components of the broth are:

Tryptose	20.0	g
Lactose	5.0	g
Diphosphate hydrogen phosphate, K_2HPO_4	2.75	g
Potassium dihydrogen phosphate, KH_2PO_4	2.75	g
Sodium chloride, NaCl	5.0	g
Sodium lauryl sulfate	0.1	g
Type II water	1	liter

Lauryl tryptose broth is also available in a prepackaged dry powder form.

5.3.2 Make lauryl tryptose broth of such strength that adding 100-mL or 10-mL portions of sample to medium will not reduce ingredient concentrations below those of the standard medium. Prepare in accordance with Table 1.

TABLE 1. PREPARATION OF LAURYL TRYPTOSE BROTH

Inoculum (mL)	Amount of Medium in Tube (mL)	Volume of Medium + Inoculum (mL)	Dehydrated Lauryl Tryptose Broth Required (g/liter)
1	10 or more	11 or more	35.6
10	10	20	71.2
10	20	30	53.4
100	50	150	106.8
100	35	135	137.1
100	20	120	213.6

5.3.3 Dispense the broth into fermentation tubes which contain inverted vials. Add an amount sufficient to cover the inverted vial, at least partially, after sterilization has taken place. Sterilize at 121°C for 12 to 15 min. The pH should be 6.8 $\pm$ 0.2 after sterilization.

5.4 Brilliant green lactose bile broth:

5.4.1 Components of the broth are:

Peptone	10.0	g
Lactose	10.0	g
Oxgall	20.0	g
Brilliant green	0.0133	g
Type II water	1	liter

This broth is also available in a prepackaged dry powder form.

5.4.2 Dispense the broth into fermentation tubes which contain inverted vials. Add an amount sufficient to cover the inverted vial, at least partially, after sterilization has taken place. Sterilize at 121°C for 12 to 15 min. The pH should be 7.2 ± 0.2 after sterilization.

5.5 Ammonium oxalate-crystal violet (Hucker's): Dissolve 2 g crystal violet (90% dye content) in 20 mL 95% ethyl alcohol, dissolve 0.8 g $(NH_4)_2C_2O_4 \cdot H_2O$ in 80 mL Type II water, mix the two solutions, and age for 24 hr before use; filter through paper into a staining bottle.

5.6 Lugol's solution, Gram's modification: Grind 1 g iodine crystals and 2 g KI in a mortar. Add Type II water, a few milliliters at a time, and grind thoroughly after each addition until solution is complete. Rinse solution into an amber glass bottle with the remaining water (using a total of 300 mL).

5.7 Counterstain: Dissolve 2.5 g safranin dye in 100 mL 95% ethyl alcohol. Add 10 mL to 100 mL Type II water.

5.8 Acetone alcohol: Mix equal volumes of ethyl alcohol, 95%, with acetone.

5.9 Gram staining kits: Commercially available kits may be substituted for 5.5, 5.6, 5.7, and 5.8.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in U.S. EPA, 1978.

6.2 Clean all glassware thoroughly with a suitable detergent and hot water, rinse with hot water to remove all traces of residual washing compound, and finally rinse with Type II water. If mechanical glassware washers are used, equip them with influent plumbing of stainless steel or other nontoxic material. Do not use copper piping to distribute Type II water. Use stainless steel or other nontoxic material for the rinse-water system.

6.2.1 Sterilize glassware, except when in metal containers, for not less than 60 min at a temperature of 170°C, unless it is known from recording thermometers that oven temperatures are uniform, under which exceptional condition use 160°C. Heat glassware in metal containers to 170°C for not less than 2 hr.

6.2.2 Sterilize sample bottles not made of plastic as above, or in an autoclave at 121°C for 15 min. Perform a sterility check on one bottle per batch.

6.2.3 If water containing residual chlorine and other halogens is to be collected, add sufficient $Na_2S_2O_3$ to clean sample bottle before sterilization to give a concentration of about 100 mg/L in the sample. To a 120-mL bottle add 0.1 mL 10% solution of $Na_2S_2O_3$ (this will neutralize a sample containing about 15 mg/L residual chlorine). Stopper bottle, cap, and sterilize by either dry or moist heat, as directed previously.

6.2.4 Collect water samples high in copper or zinc and wastewater samples high in heavy metals in sample bottles containing a chelating agent that will reduce metal toxicity. This is particularly significant when such samples are in transit for 4 hr or more. Use 372 mg/L of the tetrasodium salt of ethylenediaminetetraacetic acid (EDTA). Adjust EDTA solution to pH 6.5 before use. Add EDTA separately to sample bottle before bottle sterilization (0.3 mL 15% solution in a 120-mL bottle) or combine it with the $Na_2S_2O_3$ solution before addition.

6.3 When the sample is collected, leave ample air space in the bottle (at least 2.5 cm) to facilitate mixing by shaking, preparatory to examination. Be careful to take samples that will be representative of the water being tested and avoid sample contamination at time of collection or in period before examination.

6.4 Keep sampling bottle closed until the moment it is to be filled. Remove stopper and hood or cap as a unit, taking care to avoid soiling. During sampling, do not handle stopper or cap and neck of bottle and protect them from contamination. Hold bottle near base, fill it without rinsing, replace stopper or cap immediately, and secure hood around neck of bottle.

7.0 PROCEDURE

7.1 Presumptive stage:

7.1.1 Inoculate a series of fermentation tubes ("primary" fermentation tubes) with appropriate graduated quantities (multiples and submultiples of 1 mL) of sample. Be sure that the concentration of nutritive ingredients in the mixture of medium and added sample conforms to the requirements given in Paragraph 5.3. Use a sterile pipet for initial and subsequent transfers from each sample container. If the pipet becomes contaminated before transfers are completed, replace with a sterile pipet. Use a separate sterile pipet for transfers from each different dilution. Do not prepare dilutions in direct sunlight. Use caution when removing sterile pipets from the container; to avoid contamination, do not drag pipet tip across exposed ends of pipets or across lips and necks of dilution bottles. When removing sample, do not insert pipets more than 2.5 cm below the surface of sample or dilution. When discharging sample portions, hold pipet at an angle of about 45°, with tip touching the inside neck of the tube. The portions of sample used for inoculating lauryl-tryptose-broth fermentation tubes will vary in size and number with the character of the water under examination, but

in general use decimal multiples and submultiples of 1 mL. Use Figure 1 as a guide to preparing dilutions. After adding sample, mix thoroughly by shaking the test tube rack. Do not invert the tubes.

7.1.2 Incubate inoculated fermentation tubes at 35 ± 0.5°C. After 24 ± 2 hr shake each tube gently and examine it and, if no gas has formed and been trapped in the inverted vial, reincubate and reexamine at the end of 48 ± 3 hr. Record presence or absence of gas formation, regardless of amount, at each examination of the tubes.

7.1.3 Formation of gas in any amount in the inner fermentation tubes or vials within 48 ± 3 hr constitutes a positive presumptive test. Do not confuse the appearance of an air bubble in a clear tube with actual gas production. If gas is formed as a result of fermentation, the broth medium will become cloudy. Active fermentation may be shown by the continued appearance of small bubbles of gas throughout the medium outside the inner vial when the fermentation tube is shaken gently.

7.1.4 The absence of gas formation at the end of 48 ± 3 hr of incubation constitutes a negative test. An arbitrary limit of 48 hr for observation doubtless excludes from consideration occasional members of the coliform group that form gas very slowly and generally are of limited sanitary significance.

7.2 Confirmed stage:

7.2.1 Submit all primary fermentation tubes showing any amount of gas within 24 hr of incubation to the Confirmed Test. If active fermentation appears in the primary fermentation tube earlier than 24 hr, transfer to the confirmatory medium without waiting for the full 24-hr period to elapse. If additional primary fermentation tubes show gas production at the end of 48-hr incubation, submit these to the Confirmed Test.

7.2.2 Gently shake or rotate primary fermentation tube showing gas and do one of two things: (a) with a sterile metal loop, 3 mm in diameter, transfer one loopful of culture to a fermentation tube containing brilliant green lactose bile broth, or (b) insert a sterile wooden applicator at least 2.5 cm long into the culture, remove it promptly, and plunge it to the bottom of fermentation tube containing brilliant green lactose bile broth. Remove and discard applicator.

7.2.3 Incubate the inoculated brilliant green lactose bile broth tube for 48 ± 3 hr at 35 ± 0.5°C. Formation of gas in any amount in the inverted vial of the brilliant green lactose bile broth fermentation tube at any time within 48 ± 3 hr constitutes a positive Confirmed Test.

7.3 Completed test:

7.3.1 Use the Completed Test on positive confirmed tubes to establish definitely the presence of coliform bacteria and provide quality control data for 20% of all samples analyzed.

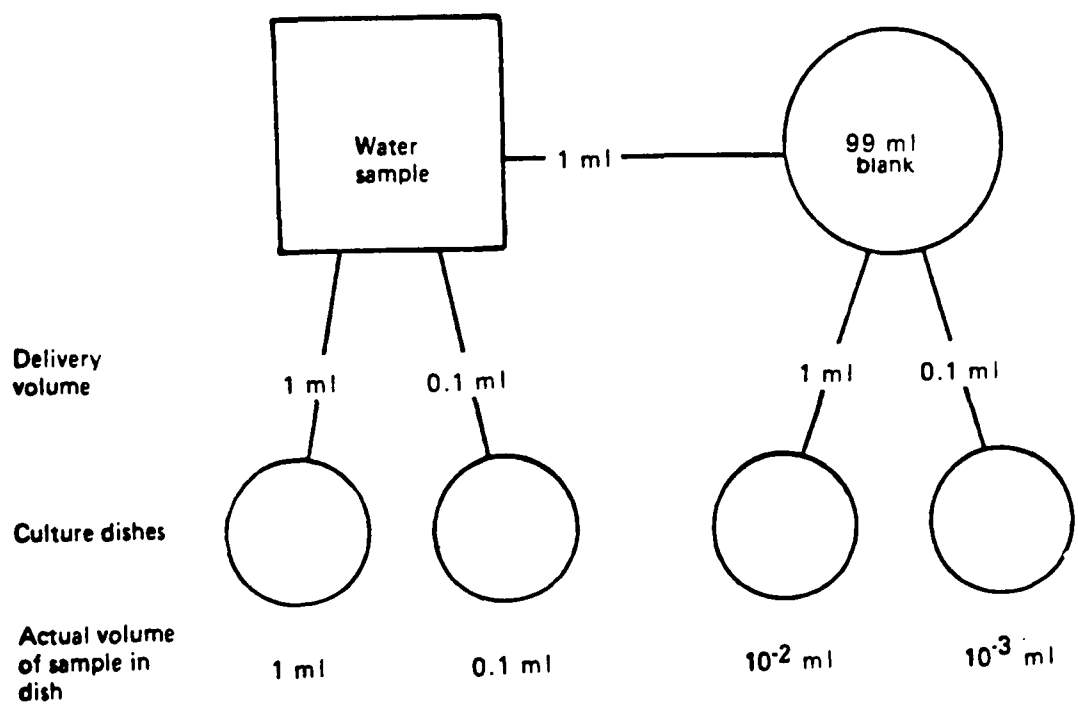


Figure 1. Preparation of dilutions.

7.3.2 Streak one or more eosin methylene blue plates from each tube of brilliant green lactose bile broth showing gas as soon as possible after the appearance of gas. Streak plates to ensure presence of some discrete colonies separated by at least 0.5 cm. Observe the following precautions when streaking plates to obtain a high proportion of successful isolations if coliform organisms are present: (a) use an inoculating needle slightly curved at the tip; (b) tap and incline the fermentation tube to avoid picking up any membrane or scum on the needle; (c) insert end of needle into the liquid in the tube to a depth of approximately 5.0 mm; and (d) streak plate with curved section of the needle in contact with the agar to avoid a scratched or torn surface.

7.3.3 Incubate plates (inverted) at 35 ± 0.5°C for 24 ± 2 hr.

7.3.4 The colonies developing on eosin methylene blue agar are called: typical (nucleated, with or without metallic sheen); atypical (opaque, unnucleated, mucoid, pink after 24-hr incubation); or negative (all others). From each of these plates, pick one or more typical well-isolated coliform colonies or, if no typical colonies are present, pick two or more colonies considered most likely to consist of organisms of the coliform group and transfer growth from each isolate to a lauryl-tryptose-broth fermentation tube and to a nutrient agar slant.

NOTE: If possible, when transferring colonies, choose well-isolated colonies and barely touch the surface of the colony with a flame-sterilized, air-cooled transfer needle to minimize the danger of transferring a mixed culture.

7.3.5 Incubate secondary broth tubes at 35 ± 0.5°C for 24 ± 2 hr; if gas is not produced within 24 ± 2 hr, reincubate and examine again at 48 ± 3 hr. Microscopically examine gram-stained preparations (see Paragraph 7.4) from those 24-hr agar slant cultures corresponding to the secondary tubes that show gas.

7.3.6 Formation of gas in the secondary tube of lauryl tryptose broth within 48 ± 3 hr and demonstration of gram-negative, non-spore-forming, rod-shaped bacteria in the agar culture constitute a satisfactory Completed Test, demonstrating the presence of a member of the coliform group.

7.4 Gram-stain procedure:

7.4.1 Prepare a light emulsion of the bacterial growth from an agar slant in a drop of Type II water on a glass slide. Air-dry or fix by passing the slide through a flame and stain for 1 min with the ammonium oxalate-crystal violet solution. Rinse the slide in tap water; apply Lugol's solution for 1 min. (See Paragraphs 5.5-5.8 for reagent.)

7.4.2 Rinse the stained slide in tap water. Decolorize for approximately 15 to 30 sec with acetone alcohol by holding slide between the fingers and letting acetone alcohol flow across the stained smear until no more stain is removed. Do not over-decolorize. Counterstain with safranin (Paragraph 5.7) for 15 sec, then rinse with tap water, blot dry with bibulous paper, and examine microscopically.

7.4.3 Cells that decolorize and accept the safranin stain are pink and defined as gram-negative in reaction. Cells that do not decolorize but retain the crystal violet stain are deep blue and are defined as gram-positive.

7.5 Computing and recording of MPN:

7.5.1 The calculated density of coliform bacteria in a sample can be obtained from the MPN table, based on the number of positive tubes in each dilution of the confirmed or completed test. Table 2 shows MPN indices and 95% confidence limits for potable water testing, and Table 3 describes the MPN indices and 95% confidence limits for general use.

TABLE 2. MPN INDEX AND 95% CONFIDENCE LIMITS FOR VARIOUS COMBINATIONS OF POSITIVE AND NEGATIVE RESULTS WHEN FIVE 10-mL PORTIONS ARE USED

Number of Tubes Giving Positive Reaction out of 5 of 10 mL each	MPN Index per 100 mL	95% Confidence Limits	
		Lower	Upper
0	<2.2	0	6.0
1	2.2	0.1	12.6
2	5.1	0.5	19.2
3	9.2	1.6	29.4
4	16	3.3	52.9
5	>16	8.0	Infinite

7.5.2 Three dilutions are necessary for the determination of the MPN index. For example (see Table 3), if five 10-mL, five 1.0-mL, and five 0.1-mL portions of the samples are used as inocula and four of the 10-mL, two of the 1-mL, and none of the 0.1-mL portions of inocula give positive results, the coded result is 4-2-0 and the MPN index is 22 per 100 mL.

7.5.3 In cases when the serial decimal dilution is other than 10, 1, and 0.1 mL, or when more than three sample volumes are used in the series, refer to the sources cited in Section 10.0, References, for the necessary density determination procedures.

7.5.4 All MPN values for water samples should be reported on the basis of a 100-mL sample.

8.0 QUALITY CONTROL

8.1 Extensive quality control procedures are provided in Part IV of U.S. EPA, 1978 (see Section 10.0, References). These procedures should be adhered to at all times.

TABLE 3. MPN INDEX FOR SERIAL DILUTIONS OF SAMPLE

Number of Tubes Giving Positive Reaction out of			MPN Index per 100 mL	95% Confidence Limits	
5 of 10 mL each	5 of 1 mL each	5 of 0.1 mL each		Lower	Upper
0	0	0	<2		
0	0	1	2	<0.5	7
0	1	0	2	<0.5	7
0	2	0	4	<0.5	11
1	0	0	2	<0.5	7
1	0	1	4	<0.5	11
1	1	0	4	<0.5	11
1	1	1	6	<0.5	15
1	2	0	6	<0.5	15
2	0	0	5	<0.5	13
2	0	1	7	1	17
2	1	0	7	1	17
2	1	1	9	2	21
2	2	0	9	2	21
2	3	0	12	3	28
3	0	0	8	1	19
3	0	1	11	2	25
3	1	0	11	2	25
3	1	1	14	4	34
3	2	0	14	4	34
3	2	1	17	5	46
3	3	0	17	5	46
4	0	0	13	3	31
4	0	1	17	5	46
4	1	0	17	5	46
4	1	1	21	7	63
4	1	2	26	9	78

Source: U.S. EPA, 1978.

(Continued on next page)

TABLE 3. MPN INDEX FOR SERIAL DILUTIONS OF SAMPLE
(Continued)

Number of Tubes Giving Positive Reaction out of			MPN Index per 100 mL	95% Confidence Limits	
5 of 10 mL each	5 of 1 mL each	5 of 0.1 mL each		Lower	Upper
4	2	0	22	7	67
4	2	1	26	9	78
4	3	0	27	9	80
4	3	1	33	11	93
4	4	0	34	12	93
5	0	0	23	7	70
5	0	1	31	11	89
5	0	2	43	15	110
5	1	0	33	11	93
5	1	1	46	16	120
5	1	2	63	21	150
5	2	0	49	17	130
5	2	1	70	23	170
5	2	2	94	28	220
5	3	0	79	25	190
5	3	1	110	31	250
5	3	2	140	37	340
5	3	3	180	44	500
5	4	0	130	35	300
5	4	1	170	43	490
5	4	2	220	57	700
5	4	3	280	90	850
5	4	4	350	120	1000
5	5	0	240	68	750
5	5	1	350	120	1000
5	5	2	540	180	1400
5	5	3	920	300	3200
5	5	4	1600	640	5800
5	5	5	>2400		

Source: U.S. EPA, 1978.

8.2 Samples must be maintained as closely as possible to original condition by careful handling and storage. Sample sites and sampling frequency should provide data representative of characteristics and variability of the water quality at that site. Samples should be analyzed immediately. They should be refrigerated at a temperature of 1-4°C and analyzed within 6 hr.

8.3 Quality control of culture media is critical to the validity of microbiological analysis. Some important factors to consider are summarized below:

8.3.1 Order media to last for only 1 yr; always use oldest stock first. Maintain an inventory of all media ordered, including a visual inspection record.

8.3.2 Hold unopened media for no longer than 2 yr. Opened media containers should be discarded after 6 mo.

8.3.3 When preparing media keep containers open as briefly as possible. Prepare media in deionized or distilled (Type II) water of proven quality. Check the pH of the media after solution and sterilization; it should be within 0.2 units of the stated value. Discard and remake if it is not.

8.3.4 Autoclave media for the minimal time specified by the manufacturer because the potential for damage increases with increased exposure to heat. Remove sterile media from the autoclave as soon as pressure is zero. Effectiveness of the sterilization should be checked weekly, using strips or ampuls of Bacillus stearothemophelus.

8.3.5 Agar plates should be kept slightly open for 15 min after pouring or removal from refrigeration to evaporate free moisture. Plates must be free of lumps, uneven surfaces, pock marks, or bubbles, which can prevent good contact between the agar and medium.

8.3.6 Avoid shaking fermentation tubes, which can entrap air in the inner vial and produce a false positive result.

8.3.7 Store fermentation tube media in the dark at room temperature or 4°C. If refrigerated, incubate overnight at room temperature to detect false positive gas bubbles.

8.3.8 Quality control checks of prepared media should include the incubation of 5% of each batch of medium for 2 days at 35°C to inspect for growth and positive/negative checks with pure culture.

8.4 Analytical quality control procedures should include:

8.4.1 Duplicate analytical runs on at least 10% of all known positive samples analyzed.

8.4.2 At least one positive control sample should be run each month for each parameter tested.

8.4.3 At least one negative (sterile) control should be run with each series of samples using buffered water and the medium batch used at the beginning of the test series and following every tenth sample. When sterile controls indicate contamination, new samples should be obtained and analyzed.

8.4.4 The Type II water used should be periodically checked for contamination.

8.4.5 For routine MPN tests, at least 5% of the positive confirmed samples should be tested by the complete test.

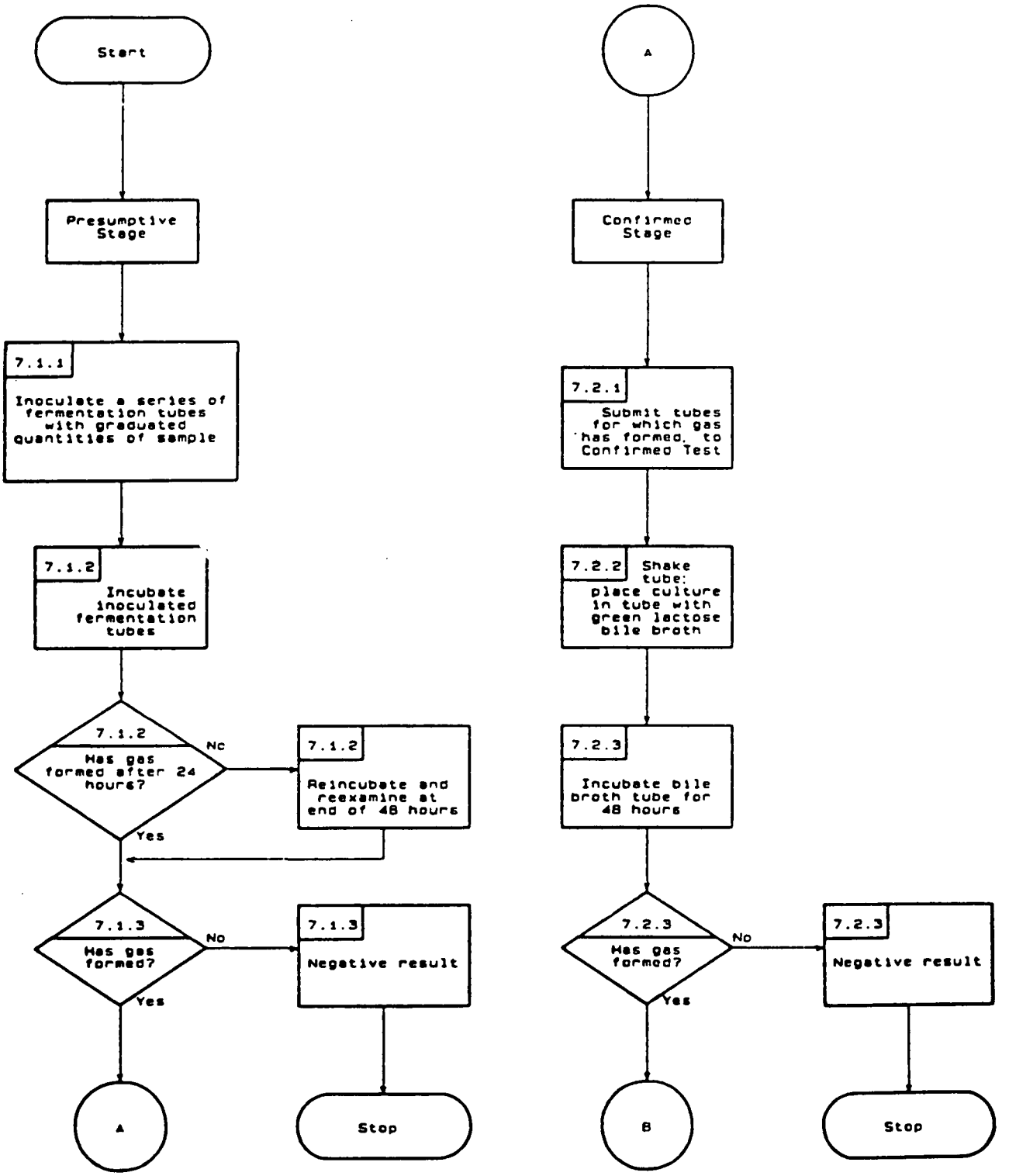
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Standard Methods for the Examination of Water and Wastewater, 15th ed. (1980).

2. U.S. Environmental Protection Agency, Microbiological Methods for Monitoring the Environment, EPA 600/8-78-017, December 1978.



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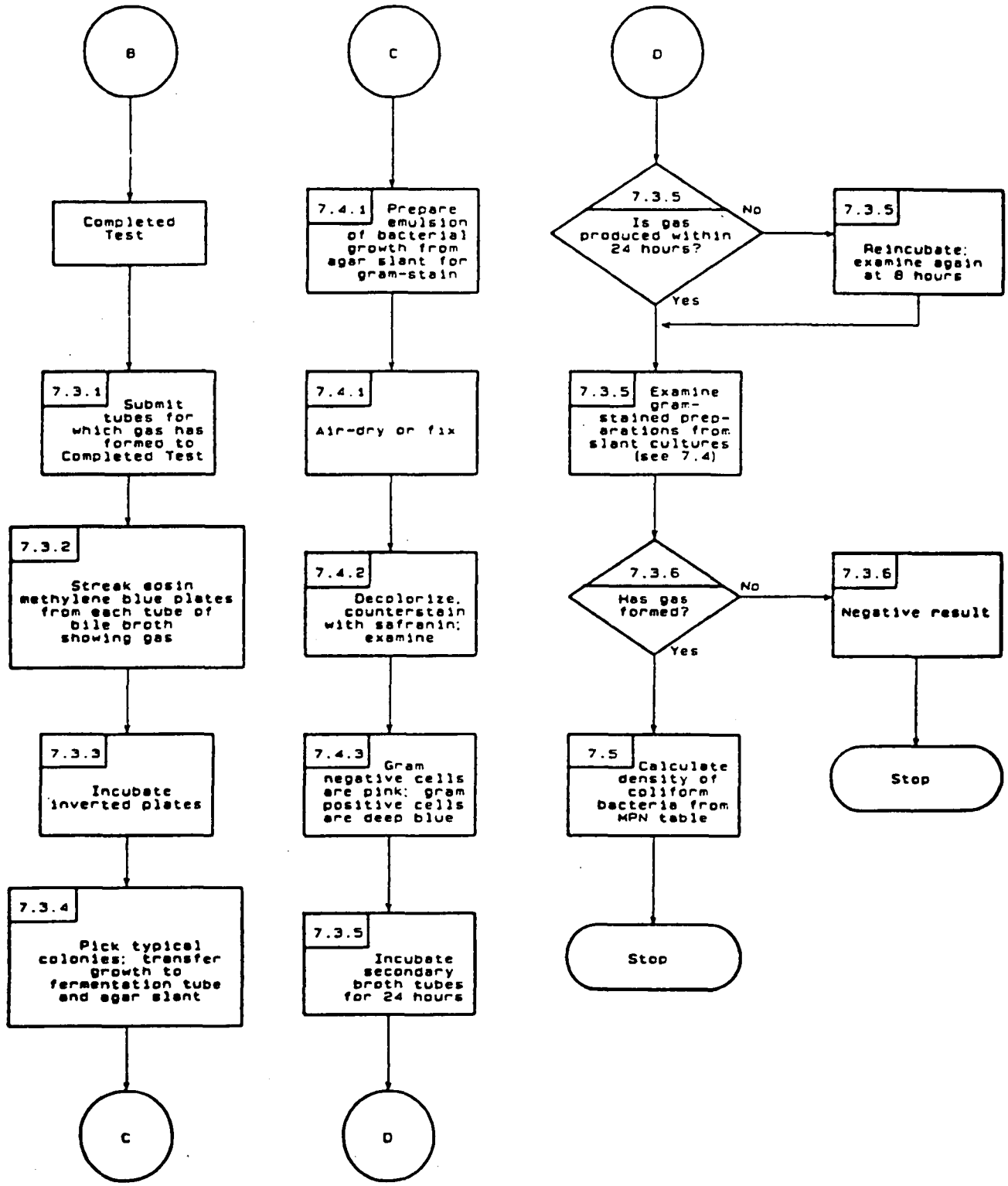

B
Completed Test
7.3.1 Submit tubes for which gas has formed to Completed Test
7.3.2 Streak eosin methylene blue plates from each tube of bile broth showing gas
7.3.3 Incubate inverted plates
7.3.4 Pick typical colonies; transfer growth to fermentation tube and agar slant
C
C
7.4.1 Prepare emulsion of bacterial growth from agar slant for gram-stain
7.4.1 Air-dry or fix
7.4.2 Decolorize, counterstain with safranin; examine
7.4.3 Gram negative cells are pink; gram positive cells are deep blue
7.3.5 Incubate secondary broth tubes for 24 hours
D
D
7.3.5 Is gas produced within 24 hours?
No
7.3.5 Reincubate; examine again at 8 hours
Yes
7.3.5 Examine gram-stained preparations from slant cultures (see 7.4)
7.3.6 Has gas formed?
No
7.3.6 Negative result
Stop
Yes
7.5 Calculate density of coliform bacteria from MPN table
Stop

METHOD 9132

TOTAL COLIFORM: MEMBRANE-FILTER TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the presence of a member of a coliform group in wastewater and ground water.

1.2 The coliform group analyzed in this procedure includes all of the organisms that produce a colony with a golden-green metallic sheen within 24 hr of inoculation.

2.0 SUMMARY OF METHOD

2.1 A predetermined amount of sample is filtered through a membrane filter which retains the bacteria found in the sample.

2.2 In the two-step enrichment procedure, the filters containing bacteria are placed on an absorbent pad saturated with lauryl tryptose broth and incubated at 35°C ± 0.5°C for 2 hr. The filters are then transferred to an absorbent pad saturated with M-Endo media or to a dish containing M-Endo agar and incubated for another 21 ± 1 hr at 35°C ± 0.5°C. Sheen colonies are then counted under magnification and reported per 100 mL of original sample.

2.3 A more detailed treatment of this method is presented in Standard Methods for the Examination of Water and Wastewater and in Microbiological Methods for Monitoring the Environment (see References, Section 10.0).

3.0 INTERFERENCES

3.1 The presence of residual chlorine or other halogen can prevent the continuation of bacterial action. To prevent this occurrence, sodium thiosulfate should be added.

3.2 Water samples high in copper, zinc, or other heavy metals can be toxic to bacteria. Chelating agents such as ethylenediaminetetraacetic acid (EDTA) should only be added when heavy metals are suspected of being present.

3.3 Turbidity caused by the presence of algae or other interfering material may not permit testing of a sample volume sufficient to yield significant results. Low coliform estimates may be caused by the presence of high numbers of noncoliforms or of toxic substances.

3.4 Samples containing large amounts of suspended solids will interfere with colony growth and with the subsequent counting of colonies on the filter membrane. When this is the case, use Method 9131.

4.0 APPARATUS AND MATERIALS

4.1 Dilution bottles or tubes:

4.1.1 Use bottles or tubes of resistant glass, preferably borosilicate glass, closed with glass stoppers or screw caps equipped with liners that do not produce toxic or bacteriostatic compounds on sterilization.

4.1.2 Do not use cotton plugs as closures. Mark graduation levels indelibly on side of dilution bottle or tube. Plastic bottles of nontoxic material and acceptable size may be substituted for glass, provided that they can be sterilized properly.

4.2 Pipets and graduated cylinders:

4.2.1 Use pipets of any convenient size, provided that they deliver the required volume accurately and quickly. The error of calibration for a given manufacturer's lot must not exceed 2.5%. Use pipets having graduations distinctly marked and with unbroken tips. Bacteriological-transfer pipets or pipets conforming to the APHA standards given in the latest edition of Standard Methods for the Examination of Dairy Products may be used. Optimally, protect the mouth end of all pipets by a cotton plug to eliminate hazards to the worker or possible sample contamination by saliva.

4.2.2 Use graduated cylinders meeting ASTM Standards (D-86 and D216) and with accuracy limits established by the National Bureau of Standards where appropriate.

4.3 Containers for culture medium:

4.3.1 Use clean borosilicate glass flasks presterilized to reduce bacterial contamination. Any size or shape of flask may be used, but Erlenmeyer flasks with metal caps, metal foil covers, or screw caps provide for adequate mixing of the medium and are convenient for storage.

4.4 Culture dishes:

4.4.1 Use Petri-type dishes, 60 by 15 mm, 50 x 12 mm, or other appropriate size. The bottoms of the dishes should be flat and large enough so that the absorbent pads for the culture nutrient will lie flat. Wrap clean culture dishes before sterilization, singly or in convenient numbers, in metal foil if sterilized by dry heat, or in suitable paper substitute when autoclaved. If glass Petri dishes are used, use borosilicate or equivalent glass. Because covers for such dishes are loose fitting, take precautions to prevent possible loss of medium by evaporation, with resultant change in medium concentration, and to maintain a humid environment for optimal colony development.

4.4.2 Disposable plastic dishes that are tight fitting and meet the specifications noted above also may be used. Suitable sterile plastic dishes are available commercially.

4.5 Filtration units:

4.5.1 The filter-holding assembly (constructed of glass, autoclavable plastic, porcelain, or any noncorrosive bacteriologically inert metal) consists of a seamless funnel fastened by a locking device or held in place by magnetic force or gravity. The design should be such that the membrane filter will be held securely on the porous plate of the receptacle without mechanical damage and all fluid will pass through the membrane during filtration.

4.5.2 Separately wrap the two parts of the assembly in heavy wrapping paper for sterilization by autoclaving and storage until use. Alternatively, treat unwrapped parts by ultraviolet radiation before using them. Field units may be sanitized by igniting methyl alcohol or immersing in boiling water for 5 min. Do not ignite plastic parts.

4.5.3 For filtration, mount receptacle of filter-holding assembly in a 1-liter filtering flask with a side tube or other suitable device such that a pressure differential can be exerted on the filter membrane. Connect flask to an electric vacuum pump, a filter pump operating on water pressure, a hand aspirator, or other means of securing pressure differential. Connect an additional flask between filtering flask and vacuum source to trap carry-over water.

4.6 Filter membranes:

4.6.1 Use membrane filters with a rated pore diameter such that there is complete retention of coliform bacteria (0.45 $\pm$ 0.02 um). Use only those filter membranes that have been found, through adequate quality control testing and certification by the manufacturer, to exhibit full retention of the organisms to be cultivated, stability in use, freedom from chemical extractables inimical to the growth and development of bacteria, a satisfactory speed of filtration, no significant influence on medium pH, and no increase in number of confluent colonies or spreaders. Preferably, use membranes grid-marked in such a manner that bacterial growth is neither inhibited nor stimulated along the grid lines. Store membrane filters held in stock in an environment without extremes of temperature and humidity. Obtain no more than a year's supply at any one time.

4.6.2 If presterilized membrane filters are to be used, use those for which the manufacturer has certified that the sterilization technique has neither induced toxicity nor altered the chemical or physical properties of the membrane. If the membranes are sterilized in the laboratory, remove the paper separators -- but not the absorbent paper pads -- from the packaged filters. Divide filters into groups of 10 to 12, or other convenient units, and place in 10-cm Petri dishes or wrap in heavy wrapping paper. Autoclave for 10 min at 121°C. At the end of the sterilization period, let the steam escape rapidly to minimize accumulation of water condensation on filters.

4.7 Absorbent pads:

4.7.1 Absorbent pads consist of disks of filter paper or other material known to be of high quality and free of sulfites or other substances that could inhibit bacterial growth. Use pads approximately 48 mm in diameter and of sufficient thickness to absorb 1.8 to 2.2 mL of medium. Presterilized absorbent pads or pads subsequently sterilized in the laboratory should release less than 1 mg total acidity (calculated as $CaCO_3$) when titrated to the phenolphthalein end point, pH 8.3, using 0.02 N NaOH. Where there is evidence of absorbent pad toxicity, presoak pads in Type II water at 121°C (in an autoclave) for 15 min, decant the water, and repackage pads in a large Petri dish for sterilization and subsequent use. Sterilize pads simultaneously with membrane filters available in resealable Kraft envelopes or separately in other suitable containers. Dry pads so they are free of visible moisture before use. See sterilization procedure described above for membrane filters.

4.7.2 As a substrate substitution for nutrient-saturated absorbent pads, 1.5% agar may be added to the total coliform M-Endo broth medium.

4.8 Forceps:

4.8.1 Forceps should be round-tipped, without corrugations on the inner sides of the tips. Sterilize before use by dipping in 95% ethyl or absolute methyl alcohol and flaming.

4.9 Incubators

4.9.1 Use incubators to provide a temperature of 35 ± 0.5°C and to maintain a high level of humidity (approximately 90% relative humidity).

4.10 Microscope and light source:

4.10.1 Count membrane-filter colonies with a magnification of 10 to 15 diameters and a light source adjusted to give maximum sheen discernment. Optimally, use a binocular wide-field dissecting microscope. However, a small fluorescent lamp with magnifier is acceptable. Use cool-white fluorescent lamps. Do not use a microscope illuminator with optical system for light concentration from an incandescent light source for coliform colony identification on Endo-type media.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 M-Endo medium:

5.2.1 Components of the medium are:

Tryptose or polypeptone	10.0 g
Thiopeptone or thiotone	5.0 g
Casitone or trypticase	5.0 g
Yeast extract	1.5 g
Lactose	12.5 g
Sodium chloride, NaCl	5.0 g
Dipotassium hydrogen phosphate, K_2HPO_4	4.375 g
Potassium dihydrogen phosphate, KH_2PO_4	1.375 g
Sodium lauryl sulfate	0.050 g
Sodium desoxycholate	0.10 g
Sodium sulfite, Na_2SO_3	2.10 g
Basic fuchsin	1.05 g
Distilled (Type II) water	1 liter

5.2.2 Rehydrate in 1 liter Type II water containing 20 mL 95% ethanol. Heat to boiling in a water bath to avoid degradation of carbohydrates, promptly remove from heat, and cool to below 45°C. Do not sterilize by autoclaving. Final pH should be between 7.1 and 7.3.

5.2.3 Store finished medium in the dark at 2 to 10°C and discard any unused medium after 96 hr. Medium is light sensitive.

NOTE: This medium may be solidified by adding 1.2% to 1.5% agar before boiling.

5.3 Lauryl tryptose broth: See Method 9131, Paragraph 5.3.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Clean all glassware thoroughly with a suitable detergent and hot water, rinse with hot water to remove all traces of residual washing compound, and finally, rinse with distilled (Type II) water. If mechanical glassware washers are used, equip them with influent plumbing of stainless steel or other nontoxic material. Do not use copper piping to distribute Type II water. Use stainless steel or other nontoxic material for the rinse-water system.

6.2.1 Sterilize glassware, except when in metal containers, for not less than 60 min at a temperature of 170°C, unless it is known from recording thermometers that oven temperatures are uniform, under which exceptional condition use 160°C. Heat glassware in metal containers to 170°C for not less than 2 hr.

6.2.2 Sterilize sample bottles not made of plastic, as above, or in an autoclave at 121°C for 15 min.

6.2.3 For plastic bottles that distort on autoclaving, use low-temperature ethylene oxide gas sterilization. If water containing residual chlorine and other halogens is to be collected, add sufficient $Na_2S_2O_3$ to clean sample bottle before sterilization to give a concentration of about 100 mg/L in the sample. To a 120-mL bottle add 0.1 mL 10% solution of $Na_2S_2O_3$ (this will neutralize a sample containing about 15 mg/L residual chlorine). Stopper bottle, cap, and sterilize by either dry or moist heat, as directed previously.

6.2.4 Collect water samples high in copper or zinc and wastewater samples high in heavy metals in sample bottles containing a chelating agent that will reduce metal toxicity. This is particularly significant when such samples are in transit for 4 hr or more. Use 372 mg/L of the tetrasodium salt of ethylenediaminetetraacetic acid (EDTA). Adjust EDTA solution to pH 6.5 before use. Add EDTA separately to sample bottle before bottle sterilization (0.3 mL 15% solution in a 120-mL bottle) or combine it with the $Na_2S_2O_3$ solution before addition.

6.3 When the sample is collected, leave ample air space in the bottle (at least 2.5 cm) to facilitate mixing by shaking, preparatory to examination. Be careful to take samples that will be representative of the water being tested and avoid sample contamination at time of collection or in period before examination.

6.4 Keep sampling bottle closed until the moment it is to be filled. Remove stopper and hood or cap as a unit, taking care to avoid soiling. During sampling, do not handle stopper or cap and neck of bottle, and protect them from contamination. Hold bottle near base, fill it without rinsing, replace stopper or cap immediately, and secure hood around neck of bottle.

6.5 Start bacteriological examination of a water sample promptly after collection to avoid unpredictable changes. If samples cannot be processed within 1 hr of collection, use an iced cooler for storage during transport to the laboratory.

6.6 Hold temperature of all stream pollution samples below 10°C during a maximum transport time of 6 hr. Refrigerate these samples upon receipt in the laboratory and process within 2 hr. When local conditions necessitate delays in delivery of samples longer than 6 hr, make field examinations using field laboratory facilities located at the site of collection or use delayed-incubation procedures.

7.0 PROCEDURES

7.1 Selection of sample size:

7.1.1 Size of sample will be governed by expected bacterial density, which in finished-water samples will be limited only by the degree of turbidity.

7.1.2 An ideal sample volume will yield growth of about 50 coliform colonies and not more then 200 colonies of all types. Examine finished waters by filtering duplicate portions of the same volume, such as 100 to 500 mL or more, or by filtering two diluted volumes. Examine other waters by filtering three different volumes, depending on the expected bacterial density. When less than 20 mL of sample (diluted or undiluted) is filtered, add a small amount of sterile dilution water to the funnel before filtration. This increase in water volume aids in uniform dispersion of the bacterial suspension over the entire effective filtering surface.

7.2 Filtration of sample:

7.2.1 Using sterile forceps, place a sterile filter over porous plate of receptacle, grid side up. Carefully place matched funnel unit over receptacle and lock it in place. Filter sample under partial vacuum. With filter still in place, rinse funnel by filtering three 20- to 30-mL portions of sterile dilution water. Unlock and remove funnel, immediately remove filter with sterile forceps, and place it on sterile pad or agar with a rolling motion to avoid entrapment of air.

7.2.2 Use sterile filtration units at the beginning of each filtration series as a minimum precaution to avoid accidental contamination. A filtration series is considered to be interrupted when an interval of 30 min or longer elapses between sample filtrations. After such interruption, treat any further sample filtration as a new filtration series and sterilize all membrane-filter holders in use.

7.2.3 Decontaminate this equipment between successive filtrations by use of flowing steam, boiling water, or, if available, an ultraviolet sterilizer. When using the UV sterilization procedure, a 2-min exposure to UV radiation is sufficient and should kill 99.9% of all bacteria. Eye protection is recommended to protect against stray radiation from a non-light-tight sterilization cabinet. This UV equipment is not commercially available and is not required, although its use is recommended.

7.3 Two-step enrichment technique:

7.3.1 Place a sterile absorbent pad in the upper half of a sterile culture dish and pipet enough enrichment medium (1.8 to 2.0 mL lauryl tryptose broth) to saturate pad. Carefully remove any surplus liquid.

Aseptically place filter through which the sample has been passed on pad. Incubate filter, without inverting dish, for 1.5 to 2 hr at 35 ± 0.5°C in an atmosphere of at least 90% relative humidity.

7.3.2 Remove enrichment culture from incubator, lift filter from enrichment pad, and roll it onto the agar surface. Incorrect filter placement is at once obvious, because patches of unstained membrane indicate entrapment of air. Where such patches occur, carefully reseat filter on agar surface. If the liquid medium is used, prepare final culture by removing enrichment culture from incubator and separating the dish halves. Place a fresh sterile pad in bottom half of dish and saturate it with 1.8 to 2.0 mL of final M-Endo medium. Transfer filter, with same precautions as above, to new pad. Discard used pad. With either the agar or the liquid medium, invert dish and incubate for 20 to 22 hr at 35 ± 0.5°C.

7.4 Counting:

7.4.1 The typical coliform colony has a pink to dark-red color with a metallic surface sheen. The sheen area may vary in size from a small pinhead to complete coverage of the colony surface. Count sheen colonies with the aid of a low-power (10 to 15 magnifications) binocular wide-field dissecting microscope or other optical device, with a cool-white fluorescent light source directed above and as nearly perpendicular as possible to the plane of the filter. The total count of colonies (coliform and noncoliform) on Endo-type medium has no relation to the total number of bacteria present in the original sample and, so far as is known, no significance can be inferred or correlation made with the quality of the water sample.

7.5 Calculation of coliform density:

7.5.1 Report coliform density as (total) coliforms/100 mL. Compute the count, using membrane filters with 20 to 80 coliform colonies and not more than 200 colonies of all types per membrane, by the following equation:

$$\text{(Total) coliform colonies/100 mL} = \frac{\text{coliform colonies counted} \times 100}{\text{mL sample filtered}}$$

7.5.2 **Water of drinking-water quality:**

7.5.2.1 With water of good quality, the number of coliform colonies will be less than 20 per membrane. In this event, count all coliform colonies and use the formula given above to obtain coliform density.

7.5.2.2 If confluent growth occurs, that is, growth covering either the entire filtration area of the membrane or a portion thereof, and colonies are not discrete, report results as "confluent growth with or without coliforms." If the total number of bacterial

colonies, coliforms plus noncoliforms, exceeds 200 per membrane, or if the colonies are too indistinct for accurate counting, report results as "too numerous to count" (TNTC). In either case, request a new sample and select more appropriate volumes to be filtered per membrane, remembering that the standard drinking-water portion is 100 mL. Thus, instead of filtering 100 mL per membrane, 50-mL portions may be filtered through each of two membranes, 25-mL portions may be filtered through each of four membranes, etc. Total the coliform counts observed on the membranes and report as number per 100 mL.

7.5.3 **Water of other than drinking-water quality:**

7.5.3.1 As with potable water samples, if no filter has a coliform count falling in the ideal range, total the coliform counts on all filters and report as number per 100 mL. For example, if duplicate 50-mL portions were examined and the two membranes had five and three coliform colonies, respectively, report the count as eight coliform colonies per 100 mL, i.e.,

$$\frac{(5 + 3) \times 100}{(50 + 50)}$$

7.5.3.2 Similarly, if 50-, 25-, and 10-mL portions were examined and the counts were 15, 6, and 1 coliform colonies, respectively, report the count as 25/100 mL, i.e.,

$$\frac{(15 + 6) \times 100}{(50 + 25 + 10)}$$

7.5.3.3 On the other hand, if 10-, 1.0-, and 0.1-mL portions were examined with counts of 40, 9, and 1 coliform colonies respectively, select only the 10-mL portion for calculating the coliform density because this filter had a coliform count falling in the ideal range. The result is 400/100 mL, i.e.,

$$\frac{(40 \times 100)}{10}$$

In this last example, if the membrane with 40 coliform colonies also had a total bacterial colony count greater than 200, report the coliform count as 400/100 mL.

7.5.3.4 Report confluent growth or membranes with colonies too numerous to count, as described in 7.5.2, above. Request a new sample and select more appropriate volumes for filtration.

7.5.4 **Statistical reliability of membrane filter results:** Although the statistical reliability of the membrane filter technique is greater than that of the MPN procedure, membrane counts really are not absolute numbers. Table 1 illustrates some 95% confidence limits.

TABLE 1. 95% CONFIDENCE LIMITS FOR MEMBRANE-FILTER RESULTS USING 100-mL SAMPLE

Number of Coliform Colonies Counted	95% Confidence Limits	
	Lower	Upper
1	0.05	3.0
2	0.35	4.7
3	0.81	6.3
4	1.4	7.7
5	2.0	9.2

8.0 QUALITY CONTROL

8.1 Extensive quality control procedures are provided in Part IV of U.S. EPA, 1978 (see Section 10.0, References). These procedures should be adhered to at all times.

8.2 Samples must be maintained as closely as possible to original condition by careful handling and storage. Sample sites and sampling frequency should provide data representative of characteristics and variability of the water quality at that site. Samples should be analyzed immediately. If this is not practical, they should be refrigerated at a temperature of 1-4°C and analyzed within 6 hr.

8.3 Quality control of culture media is critical to the validity of microbiological analysis. Some important factors to consider are summarized below:

8.3.1 Order media to last for only 1 yr; always use oldest stock first. Maintain an inventory of all media ordered, including a visual inspection record.

8.3.2 Hold unopened media for no longer than 2 yr. Opened media containers should be discarded after 6 mo.

8.3.3 When preparing media, keep containers open as briefly as possible. Prepare media in deionized or distilled (Type II) water of proven quality. Check the pH of the media after solution and sterilization; it should be within 0.2 units of the stated value. Discard and remake if it is not.

8.3.4 Autoclave media for the minimal time specified by the manufacturer, because the potential for damage increases with increased exposure to heat. Remove sterile media from the autoclave as soon as pressure is zero. Effectiveness of the sterilization should be checked weekly, using strips or ampuls of Bacillus stearothemophelus.

8.3.5 Agar plates should be kept slightly open for 15 min after pouring or removal from refrigeration to evaporate free moisture. Plates must be free of lumps, uneven surfaces, pock marks, or bubbles, which can prevent good contact between the agar and medium.

8.3.6 Quality control checks of prepared media should include the incubation of 5% of each batch of medium for 2 days at 35°C to inspect for growth and positive/negative checks with pure culture.

8.4 Analytical quality control procedures should include:

8.4.1 Duplicate analytical runs on at least 10% of all known positive samples analyzed.

8.4.2 At least one positive control sample should be run each month for each parameter tested.

8.4.3 At least one negative (sterile) control should be run with each series of samples using buffered water and the medium batch used at the beginning of the test series and following every tenth sample. When sterile controls indicate contamination, new samples should be obtained and analyzed.

8.4.4 The Type II water used should be periodically checked for contamination.

8.5 Quality control specifications for membrane filters:

8.5.1 Membrane filters can be purchased sterile or packaged for sterilization. They can be sterilized by autoclaving, ethylene oxide, or irradiation. Membrane manufacturers should certify that their membranes meet stated specifications on sterility, retention, recovery, pore size, flow rate, pH, total acidity, phosphate, and other extractables.

8.5.2 Membrane performance should be tested to ensure proper results. Each lot ordered should be inspected for proper shape, grid lines, diffusability, and correct colony development. Membranes containing sizable areas with no colony development are questionable.

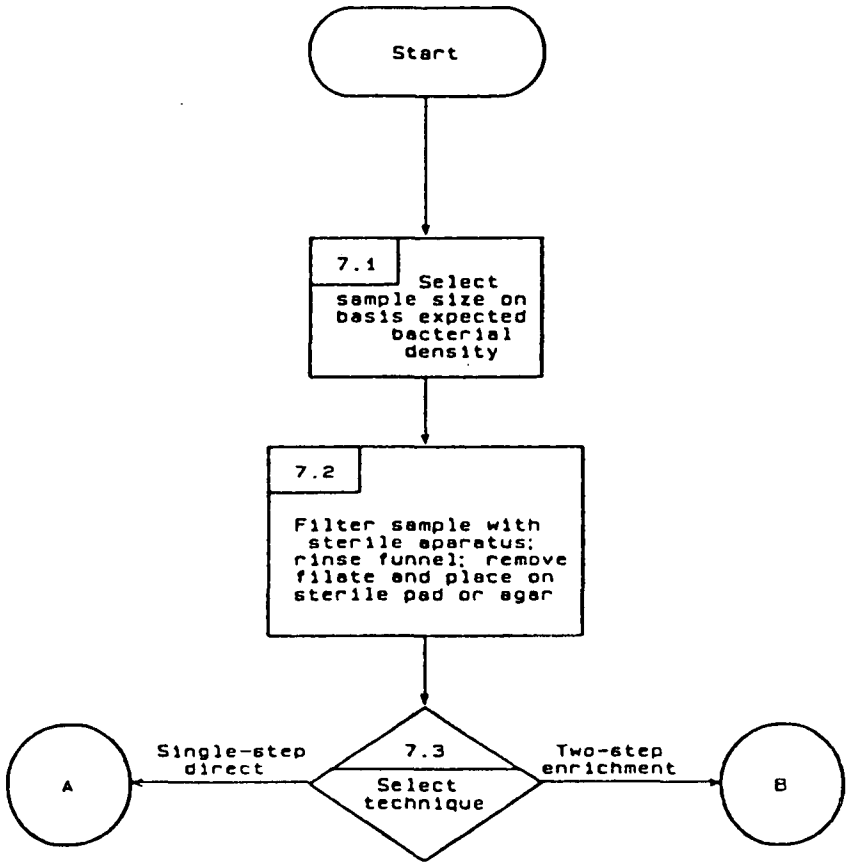
9.0 METHOD PERFORMANCE

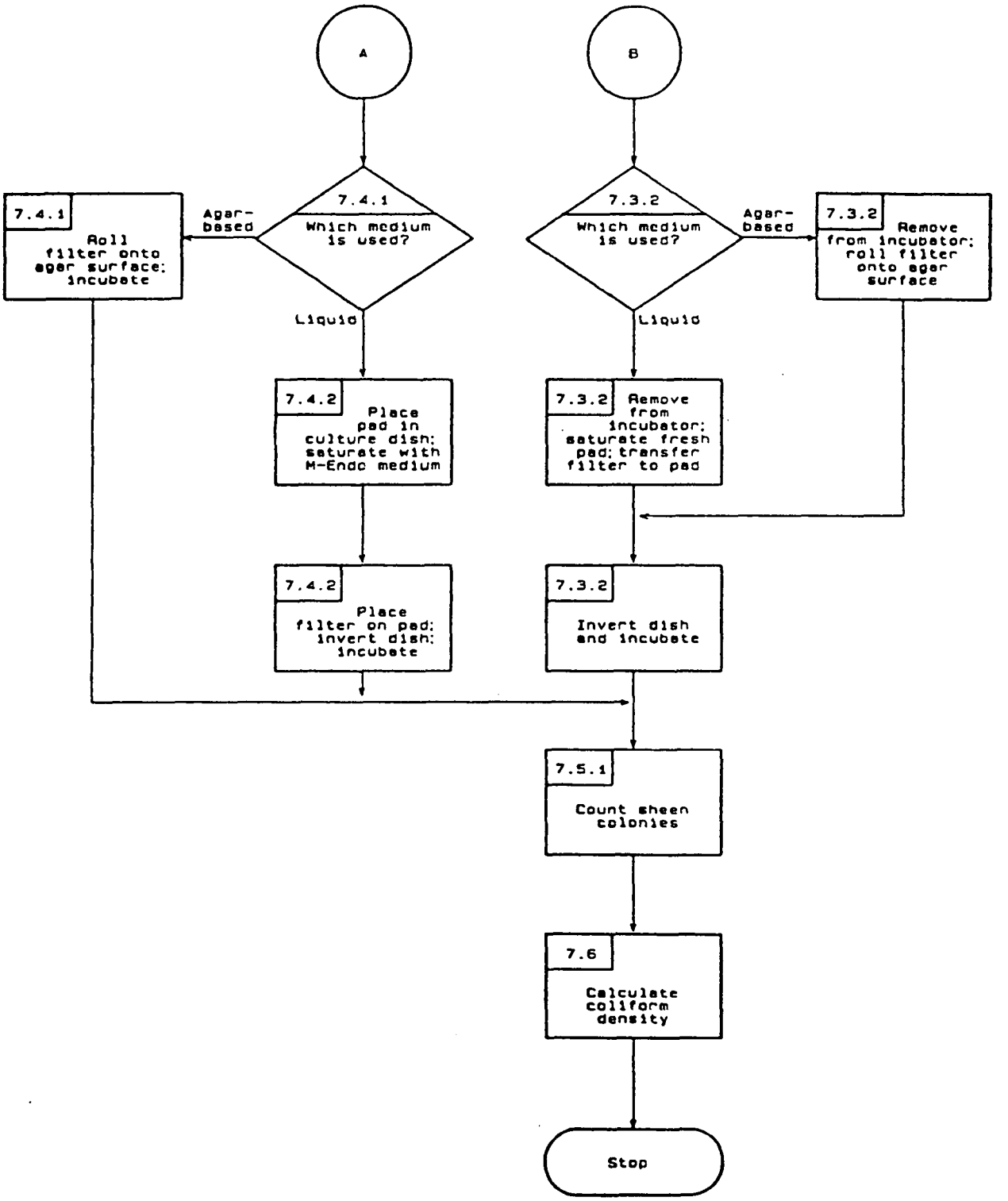
9.1 No data provided.

10.0 REFERENCES

1. Standard Methods for the Examination of Water and Wastewater, 15th ed.

2. Bordner, R.H., et al., Microbiological Methods for Monitoring the Environment, Environmental Monitoring and Support Laboratory, U.S. EPA, Cincinnati, OH, EPA-600/8-78-017, 1978.


Start
7.1
Select sample size on basis expected bacterial density
7.2
Filter sample with sterile aparatus; rinse funnel; remove filate and place on sterile pad or agar
7.3
Select technique
Single-step direct
Two-step enrichment
A
B


A
B
7.4.1
Which medium is used?
Agar-based
Liquid
7.4.1
Roll filter onto agar surface; incubate
7.4.2
Place pad in culture dish; saturate with M-Endo medium
7.4.2
Place filter on pad; invert dish; incubate
7.3.2
Which medium is used?
Agar-based
Liquid
7.3.2
Remove from incubator; roll filter onto agar surface
7.3.2
Remove from incubator; saturate fresh pad; transfer filter to pad
7.3.2
Invert dish and incubate
7.5.1
Count sheen colonies
7.6
Calculate coliform density
Stop

METHOD 9200

NITRATE

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the analysis of ground water, drinking, surface, and saline waters, and domestic and industrial wastes. Modification can be made to remove or correct for turbidity, color, salinity, or dissolved organic compounds in the sample.

1.2 The applicable range of concentration is 0.1 to 2 mg NO_3-N per liter of sample.

2.0 SUMMARY OF METHOD

2.1 This method is based upon the reaction of the nitrate ion with brucine sulfate in a 13 N H_2SO_4 solution at a temperature of 100°C. The color of the resulting complex is measured at 410 nm. Temperature control of the color reaction is extremely critical.

3.0 INTERFERENCES

3.1 Dissolved organic matter will cause an off color in 13 N H_2SO_4 and must be compensated for by additions of all reagents except the brucine-sulfanilic acid reagent. This also applies to natural color, not due to dissolved organics, that is present.

3.2 If the sample is colored or if the conditions of the test cause extraneous coloration, this interference should be corrected by running a concurrent sample under the same conditions but in the absence of the brucine-sulfanilic acid reagent.

3.3 Strong oxidizing or reducing agents cause interference. The presence of oxidizing agents may be determined by a residual chlorine test; reducing agents may be detected with potassium permanganate.

3.3.1 Oxidizing agents' interference is eliminated by the addition of sodium arsenite.

3.3.2 Reducing agents may be oxidized by addition of H_2O_2.

3.4 Ferrous and ferric iron and quadrivalent manganese give slight positive interferences, but in concentrations less than 1 mg/L these are negligible.

3.5 Uneven heating of the samples and standards during the reaction time will result in erratic values. The necessity for absolute control of temperature during the critical color development period cannot be too strongly emphasized.

4.0 APPARATUS AND MATERIALS

4.1 Spectrophotometer or filter photometer suitable for measuring absorbance at 410 nm.

4.2 Sufficient number of 40- to 50-mL glass sample tubes for reagent blanks, standards, and samples.

4.3 Neoprene-coated wire racks to hold sample tubes.

4.4 Water bath suitable for use at 100°C. This bath should contain a stirring mechanism so that all tubes are at the same temperature and should be of sufficient capacity to accept the required number of tubes without a significant drop in temperature when the tubes are immersed.

4.5 Water bath suitable for use at 10-15°C.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Sodium chloride solution (30%): Dissolve 300 g NaCl in Type II water and dilute to 1 liter.

5.3 Sulfuric acid solution: Carefully add 500 mL concentrated H_2SO_4 to 125 mL Type II water. Cool and keep tightly stoppered to prevent absorption of atmospheric moisture.

5.4 Brucine-sulfanilic acid reagent: Dissolve 1 g brucine sulfate -- $(C_{23}H_{26}N_2O_4)_2 \cdot H_2SO_4 \cdot 7H_2O$ -- and 0.1 g sulfanilic acid ($NH_2C_6H_4SO_3H \cdot H_2O$) in 70 mL hot Type II water. Add 3 mL concentrated HCl, cool, mix, and dilute to 100 mL with Type II water. Store in a dark bottle at 5°C. This solution is stable for several months; the pink color that develops slowly does not affect its usefulness. Mark bottle with warning, **"CAUTION: Brucine Sulfate is toxic; do not ingest."**

5.5 Potassium nitrate stock solution (1.0 mL = 0.1 mg NO_3-N): Dissolve 0.7218 g anhydrous potassium nitrate (KNO_3) in Type II water and dilute to 1 liter in a volumetric flask. Preserve with 2 mL chloroform per liter. This solution is stable for at least 6 mon.

5.6 Potassium nitrate standard solution (1.0 mL = 0.001 mg NO_3-N): Dilute 10.0 mL of the stock solution (5.5) to 1 liter in a volumetric flask. This standard solution should be prepared fresh weekly.

5.7 Acetic acid (1+3): Dilute 1 volume glacial acetic acid (CH_3COOH) with 3 volumes of Type II water.

5.8 Sodium hydroxide (1 N): Dissolve 40 g of NaOH in Type II water. Cool and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Analysis should be done as soon as possible. If analysis can be done within 24 hr, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hr, they should be preserved with sulfuric acid (2 mL/L concentrated H_2SO_4) and refrigerated.

7.0 PROCEDURE

7.1 Adjust the pH of the samples to approximately 7 with acetic acid (Paragraph 5.7) or sodium hydroxide (Paragraph 5.8). If necessary, filter to remove turbidity. Sulfuric acid can be used in place of acetic acid, if preferred.

7.2 Set up the required number of sample tubes in the rack to handle reagent blank, standards, and samples. Space tubes evenly throughout the rack to allow for even flow of bath water between the tubes. This should assist in achieving uniform heating of all tubes.

7.3 If it is necessary to correct for color or dissolved organic matter which will cause color on heating, run a set of duplicate samples to which all reagents, except the brucine-sulfanilic acid, have been added.

7.3.1 Add 0.5 mL brucine-sulfanilic acid reagent (Paragraph 5.4) to each tube (except the interference control tubes) and carefully mix by swirling; then place the rack of tubes in the 100°C water bath for exactly 25 min.

CAUTION: Immersion of the tube rack into the bath should not decrease the temperature of the bath by more than 1-2°C. In order to keep this temperature decrease to an absolute minimum, flow of bath water between the tubes should not be restricted by crowding too many tubes into the rack. If color development in the standards reveals discrepancies in the procedure, the operator should repeat the procedure after reviewing the temperature control steps.

7.4 Pipet 10.0 mL of standards and samples or an aliquot of the samples diluted to 10.0 mL into the sample tubes.

7.5 If the samples are saline, add 2 mL of the 30% sodium chloride solution (Paragraph 5.2) to the reagent blank, standards, and samples. For freshwater samples, sodium chloride solution may be omitted. Mix contents of tubes by swirling and place rack in cold-water bath (0-10°C).

7.6 Pipet 10.0 mL of sulfuric acid solution (Paragraph 5.3) into each tube and mix by swirling. Allow tubes to come to thermal equilibrium in the cold bath. Be sure that temperatures have equilibrated in all tubes before continuing.

7.7 Remove rack of tubes from the hot-water bath, immerse in the cold-water bath, and allow to reach thermal equilibrium (20-25°C).

7.8 Read absorbance against the reagent blank at 410 nm using a 1-cm or longer cell.

7.9 Calculation:

7.9.1 Obtain a standard curve by plotting the absorbance of standards run by the above procedure against mg/L NO_3-N. (The color reaction does not always follow Beer's law.)

7.9.2 Subtract the absorbance of the sample without the brucine-sulfanilic reagent from the absorbance of the sample containing brucine-sulfanilic acid and determine mg/L NO_3-N. Multiply by an appropriate dilution factor if less than 10 mL of sample is taken.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Linear calibration curves must be composed of a minimum of a blank and five standards. A set of standards must be included with each batch of samples.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Verify calibration with an independently prepared check standard every 15 samples.

8.5 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

9.1 Twenty-seven analysts in fifteen laboratories analyzed natural-water samples containing exact increments of inorganic nitrate, with the following results:

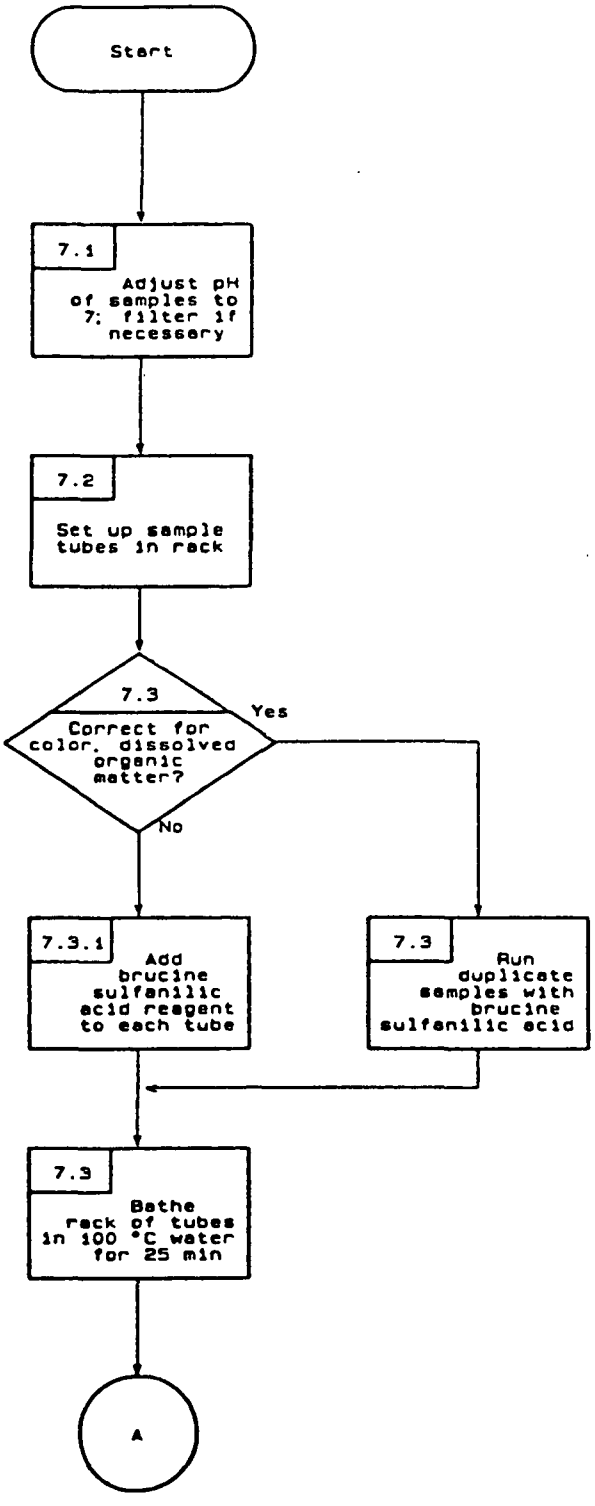
Increment as Nitrogen, Nitrate (mg/L N)	Precision as Standard Deviation (mg/L N)	Accuracy as Bias (%)	Accuracy as Bias (mg/L N)
0.16	0.092	-6.79	-0.01
0.19	0.083	+8.30	+0.02
1.08	0.245	+4.12	+0.04
1.24	0.214	+2.82	+0.04

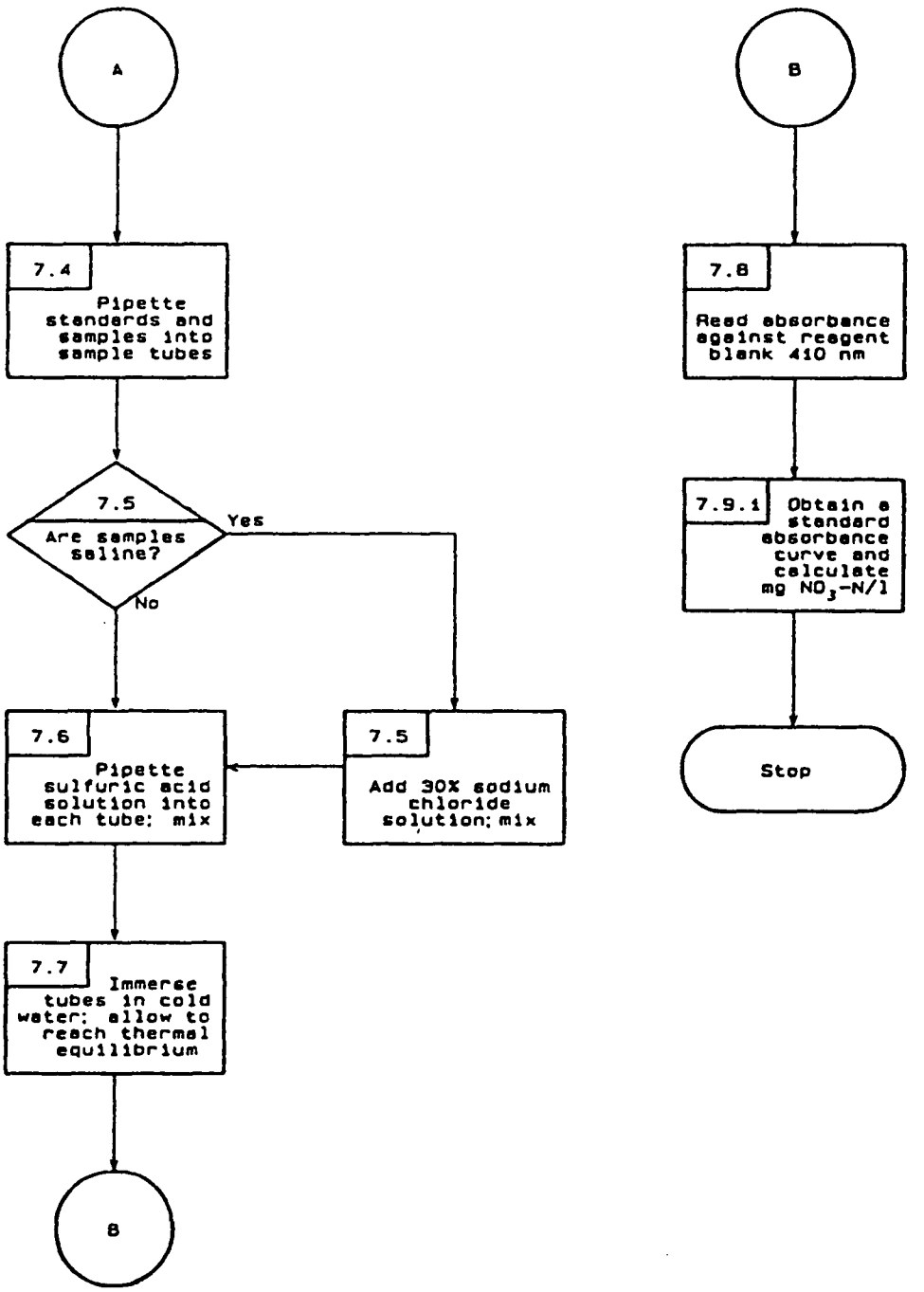
10.0 REFERENCES

1. Annual Book of ASTM Standards, Part 31, "Water," Standard D992-71, p. 363 (1976).

2. Jenkins, D. and L. Medsken, "A Brucine Method for the Determination of Nitrate in Ocean, Estuarine, and Fresh Water," Anal.Chem., 36, p. 610 (1964).

3. Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 427, Method 419D (1975).


Start
7.1
Adjust pH of samples to 7; filter if necessary
7.2
Set up sample tubes in rack
7.3
Correct for color, dissolved organic matter?
Yes
No
7.3.1
Add brucine sulfanilic acid reagent to each tube
7.3
Run duplicate samples with brucine sulfanilic acid
7.3
Bathe rack of tubes in 100 °C water for 25 min
A


A
7.4
Pipette standards and samples into sample tubes
7.5
Are samples saline?
Yes
No
7.6
Pipette sulfuric acid solution into each tube; mix
7.5
Add 30% sodium chloride solution; mix
7.7
Immerse tubes in cold water; allow to reach thermal equilibrium
B
B
7.8
Read absorbance against reagent blank 410 nm
7.9.1
Obtain a standard absorbance curve and calculate mg NO_3-N/l
Stop

METHOD 9250

CHLORIDE (COLORIMETRIC, AUTOMATED FERRICYANIDE AAI)

1.0 SCOPE AND APPLICATION

1.1 This automated method is applicable to ground water, drinking, surface, and saline waters, and domestic and industrial wastes. The applicable range is 1 to 250 mg Cl per liter of sample.

2.0 SUMMARY OF METHOD

2.1 Thiocyanate ion (SCN) is liberated from mercuric thiocyanate through sequestration of mercury by chloride ion to form un-ionized mercuric chloride. In the presence of ferric ion, the liberated SCN forms highly colored ferric thiocyanate in a concentration proportional to the original chloride concentration.

3.0 INTERFERENCES

3.1 No significant interferences.

4.0 APPARATUS AND MATERIALS

4.1 Automated continuous-flow analytical instrument:

4.1.1 **Sampler I.**

4.1.2 **Continuous filter.**

4.1.3 **Manifold.**

4.1.4 **Proportioning pump.**

4.1.5 **Colorimeter:** equipped with 15-mm tubular flowcell and 480-nm filters.

4.1.6 **Recorder.**

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Ferric ammonium sulfate: Dissolve 60 g of $FeNH_4(SO_4)_2 \cdot 12H_2O$ in approximately 500 mL Type II water. Add 355 mL of concentrated HNO_3 and dilute to 1 liter with Type II water. Filter.

5.3 Saturated mercuric thiocyanate: Dissolve 5 g of $Hg(SCN)_2$ in 1 liter of Type II water. Decant and filter a portion of the saturated supernatant liquid to use as the reagent and refill the bottle with distilled water.

5.4 Sodium chloride stock solution (0.0141 N NaCl): Dissolve 0.8241 g of pre-dried (140°C) NaCl in Type II water. Dilute to 1 liter in a volumetric flask (1 mL = 0.5 mg Cl).

5.4.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 mL with Type II water. The following dilutions are suggested:

Stock Solution (mL)	Concentration (mg/L)
1.0	5.0
2.0	10.0
4.0	20.0
8.0	40.0
15.0	75.0
20.0	100.0
30.0	150.0
40.0	200.0
50.0	250.0

Choose three of the nine standard concentrations in such a way that the chosen standards will bracket the expected concentration range of the sample.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 No special requirements for preservation.

7.0 PROCEDURE

7.1 No advance sample preparation is required. Set up manifold, as shown in Figure 1. For water samples known to be consistently low in chloride content, it is advisable to use only one Type II water intake line.

7.2 Allow both colorimeter and recorder to warm up for 30 min. Run a baseline with all reagents, feeding Type II water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

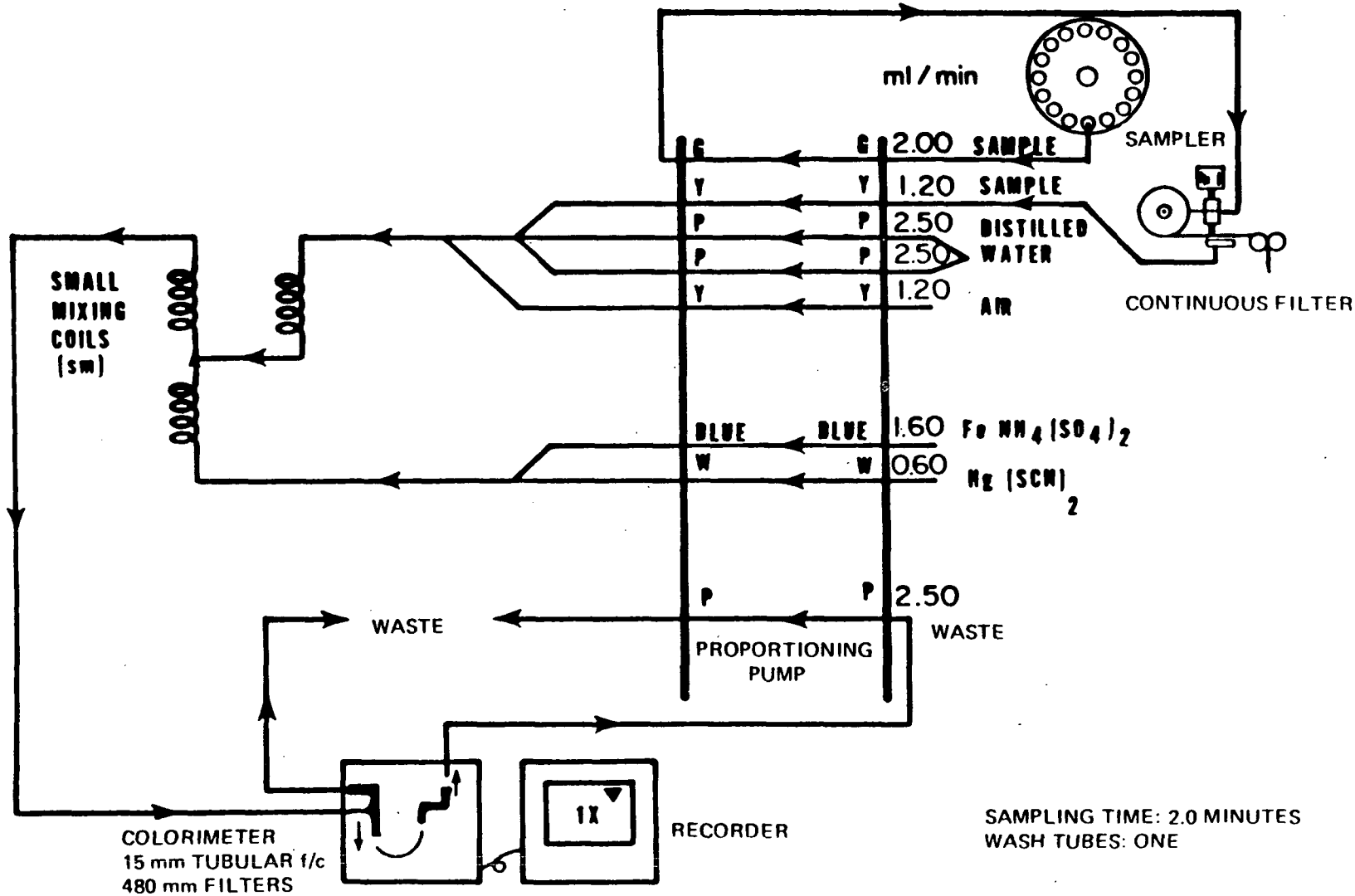


FIGURE 1. CHLORIDE MANIFOLD AA-I

7.3 Place Type II water wash tubes in alternate openings in sampler and set sample timing at 2.0 min.

7.4 Place working standards in sampler in order of decreasing concentrations. Complete filling of sampler tray with unknown samples.

7.5 Switch sample line from Type II water to sampler and begin analysis.

7.6 Calculation:

7.6.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Verify calibration with an independently prepared check standard every 15 samples.

8.5 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

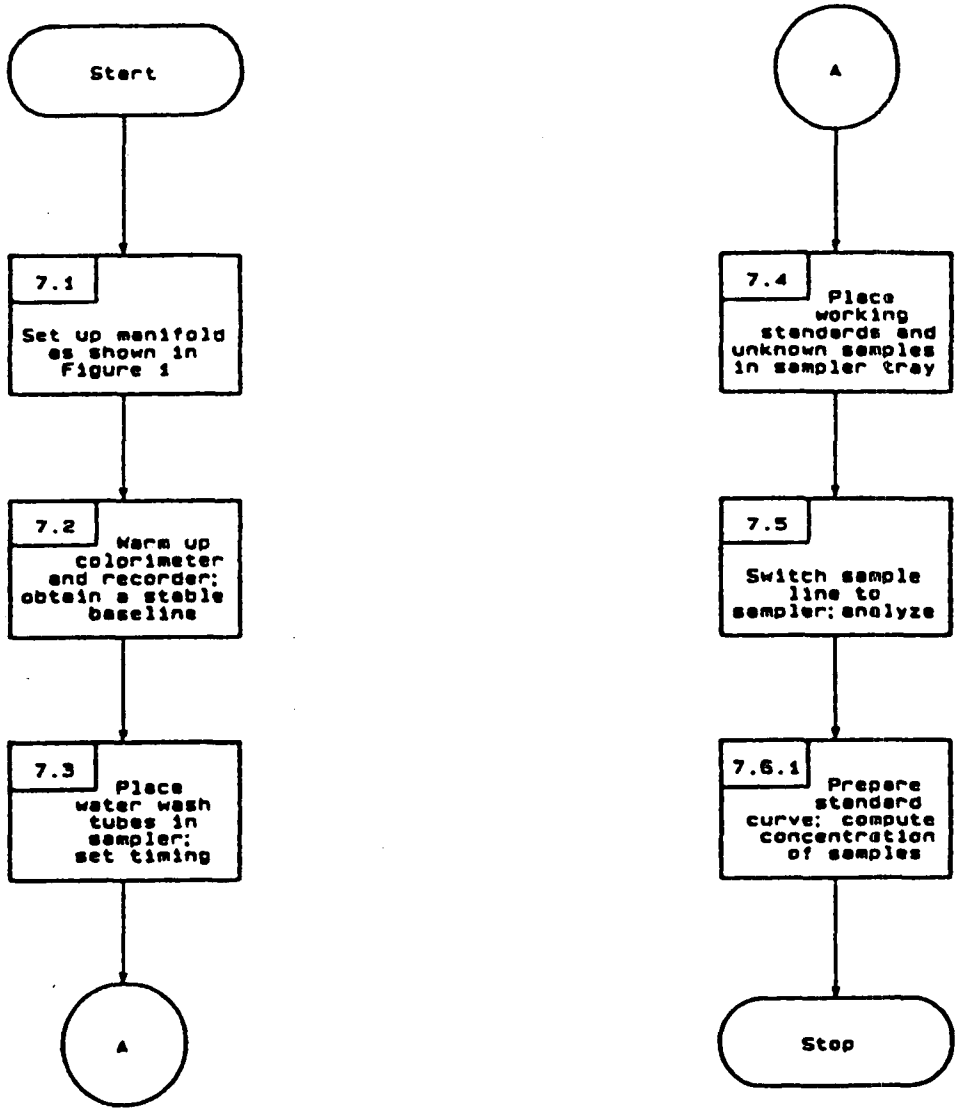
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 325.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. O'Brien, J.E., "Automatic Analysis of Chlorides in Sewage," Waste Engr., 33, 670-672 (Dec. 1962).

2. Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 613, Method 602 (1975).


Start
7.1
Set up manifold as shown in Figure 1
7.2
Warm up colorimeter and recorder; obtain a stable baseline
7.3
Place water wash tubes in sampler; set timing
A
A
7.4
Place working standards and unknown samples in sampler tray
7.5
Switch sample line to sampler; analyze
7.6.1
Prepare standard curve; compute concentration of samples
Stop

METHOD 9251

CHLORIDE (COLORIMETRIC, AUTOMATED FERRICYANIDE AAII)

1.0 SCOPE AND APPLICATION

1.1 This automated method is applicable to ground water, drinking, surface, and saline waters, and domestic and industrial wastes. The applicable range is 1-200 mg Cl^- per liter of sample.

2.0 SUMMARY OF METHOD

2.1 Thiocyanate ion (SCN) is liberated from mercuric thiocyanate through sequestration of mercury by chloride ion to form un-ionized mercuric chloride. In the presence of ferric ion, the liberated SCN forms highly colored ferric thiocyanate in a concentration proportional to the original chloride concentration.

3.0 INTERFERENCES

3.1 No significant interferences.

4.0 APPARATUS AND MATERIALS

4.1 Automated continuous-flow analytical instrument:

4.1.1 Sampler I.

4.1.2 Analytical cartridge.

4.1.3 Proportioning pump.

4.1.4 Colorimeter: Equipped with 15-mm tubular flowcell and 480-nm filters.

4.1.5 Recorder.

4.1.6 Digital printer (optional).

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Mercuric thiocyanate solution: Dissolve 4.17 g of $Hg(SCN)_2$ in 500 mL methanol. Dilute to 1 liter with methanol, mix, and filter through filter paper.

5.3 Ferric nitrate solution, 20.2%: Dissolve 202 g of $Fe(NO_3)_3 \cdot 9H_2O$ in 500 mL of Type II water. Add 31.5 mL concentrated nitric acid, mix, and dilute to 1 liter with Type II water.

5.4 Color reagent: Add 150 mL of mercuric thiocyanate solution (Paragraph 5.2) to 150 mL of ferric nitrate solution (Paragraph 5.3), mix, and dilute to 1 liter with Type II water. A combined color reagent is commercially available.

5.5 Sodium chloride stock solution (0.0141 N NaCl): Dissolve 0.8241 g of pre-dried (140°C) NaCl in Type II water. Dilute to 1 liter in a volumetric flask (1 mL = 0.5 mg Cl^-).

5.5.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 mL with Type II water. The following dilutions are suggested:

Stock Solution (mL)	Concentration (mg/L)
1.0	5.0
2.0	10.0
4.0	20.0
8.0	40.0
15.0	75.0
20.0	100.0
30.0	150.0
40.0	200.0

Choose three of the nine standard concentrations in such a way that the chosen standards will bracket the expected concentration range of the sample.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 No special requirements for preservation.

7.0 PROCEDURE

7.1 When particulate matter is present, the sample must be filtered prior to the determination. The sample may be centrifuged in place of filtration. Set up the manifold, as shown in Figure 1.

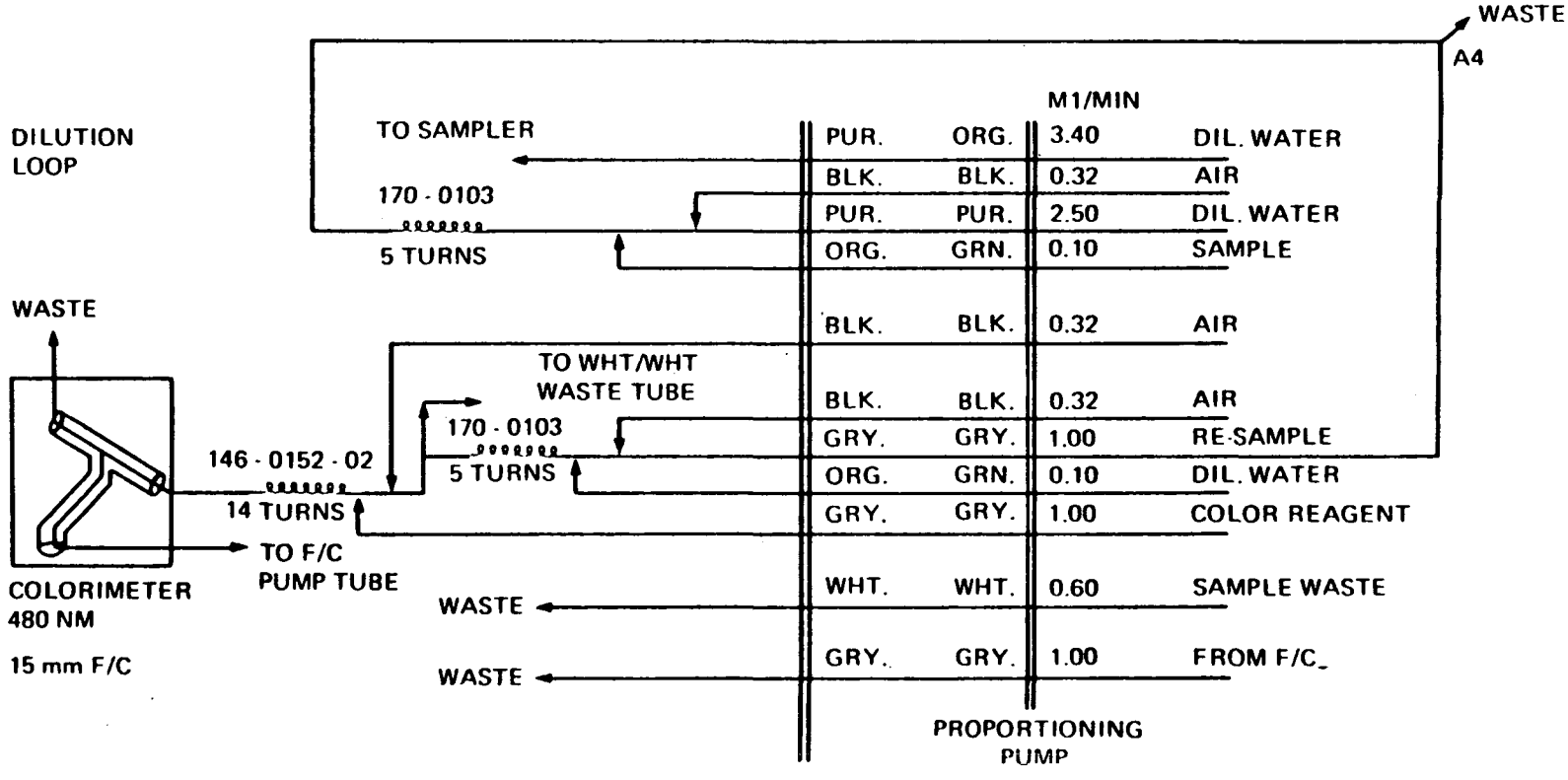


Figure 1. Chloride Manifold AA II 0-200 mg C1/L.

7.2 Allow both colorimeter and recorder to warm up for 30 min. Run a baseline with all reagents, feeding Type II water through the sample line.

7.3 Place working standards in sampler in order of decreasing concentrations. Complete filling of sampler tray with unknown samples.

7.4 When a stable baseline has been obtained, start the sampler.

7.5 Calculation: Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve. Note that this is not a linear curve, but a second order curve. (See Paragraph 8.2.)

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Verify calibration with an independently prepared check standard every 15 samples.

8.5 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

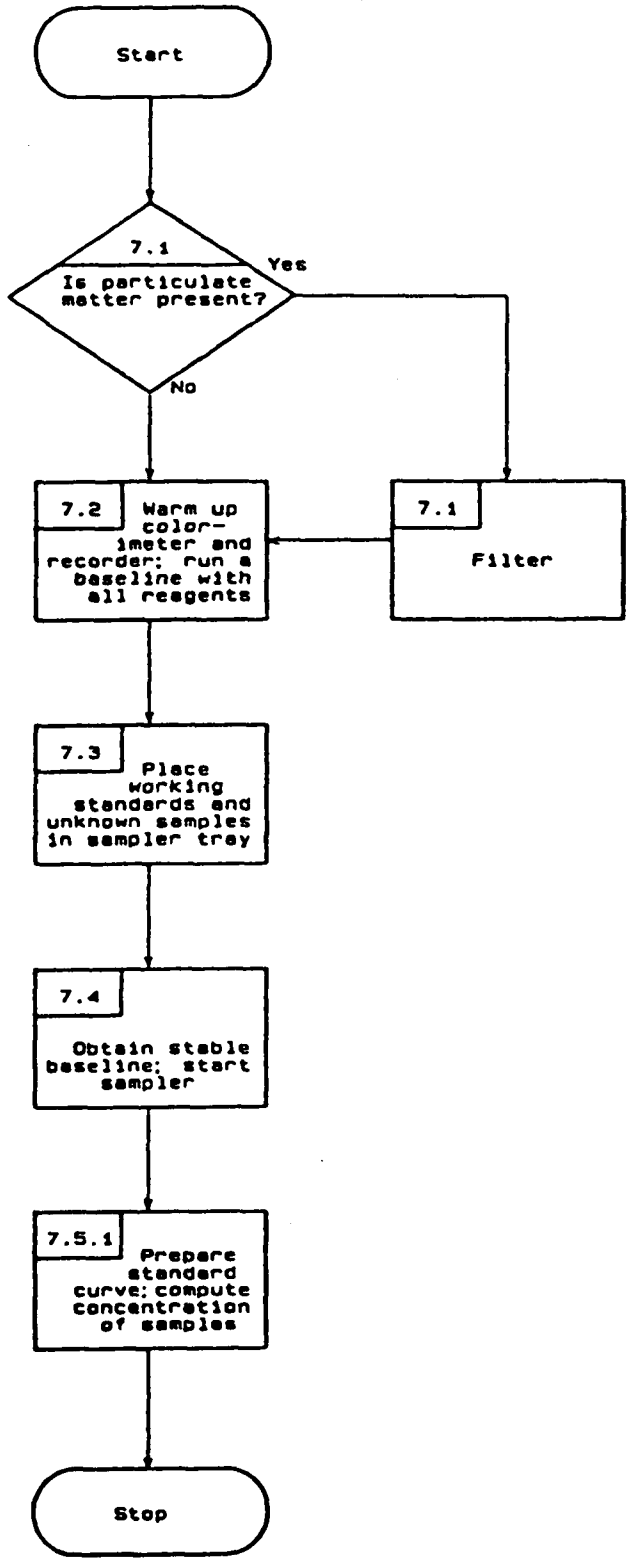
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are not available at this time.

10.0 REFERENCES

1. O'Brien, J.E., "Automatic Analysis of Chlorides in Sewage," Waste Engr., 33, 670-672 (Dec. 1962).

2. Technicon AutoAnalyzer II, Industrial Method No. 99-70W, Technicon Industrial Systems, Tarrytown, New York, 10591 (Sept. 1973).


Start
7.1
Is particulate matter present?
Yes
No
7.2
Warm up color-imeter and recorder; run a baseline with all reagents
7.1
Filter
7.3
Place working standards and unknown samples in sampler tray
7.4
Obtain stable baseline; start sampler
7.5.1
Prepare standard curve; compute concentration of samples
Stop

METHOD 9252A

CHLORIDE (TITRIMETRIC, MERCURIC NITRATE)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to ground water, drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 The method is suitable for all concentration ranges of chloride content; however, in order to avoid large titration volume, a sample aliquot containing not more than 10 to 20 mg Cl^- per 50 mL is used.

1.3 Automated titration may be used.

2.0 SUMMARY OF METHOD

2.1 An acidified sample is titrated with mercuric nitrate in the presence of mixed diphenylcarbazone-bromophenol blue indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex.

3.0 INTERFERENCES

3.1 Anions and cations at concentrations normally found in surface waters do not interfere. However, at the higher concentration often found in certain wastes, problems may occur.

3.2 Sulfite interference can be eliminated by oxidizing the 50 mL of sample solution with 0.5-1 mL of H_2O_2.

3.3 Bromide and iodide are also titrated with mercuric nitrate in the same manner as chloride.

3.4 Ferric and chromate ions interfere when present in excess of 10 mg/L.

4.0 APPARATUS AND MATERIALS

4.1 Standard laboratory titrimetric equipment, including 1 mL or 5 mL microburet with 0.01 mL gradations.

4.2 Class A volumetric flasks: 1 L and 100 mL.

4.3 pH Indicator paper.

4.4 Analytical balance: capable of weighing to 0.0001 g.

5.0 REAGENTS

5.1 Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the

specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Standard sodium chloride solution, 0.025 N: Dissolve 1.4613 g $\pm$ 0.0002 g of sodium chloride (dried at 600°C for 1 hr) in chloride-free water in a 1 liter Class A volumetric flask and dilute to the mark with reagent water.

5.4 Nitric acid (HNO_3) solution: Add 3.0 mL concentrated nitric acid to 997 mL of reagent water ("3 + 997" solution).

5.5 Sodium hydroxide (NaOH) solution (10 g/L): Dissolve approximately 10 g of NaOH in reagent water and dilute to 1 L with reagent water.

5.6 Hydrogen peroxide (H_2O_2): 30%.

5.7 Hydroquinone solution (10 g/L): Dissolve 1 g of purified hydroquinone in reagent water in a 100 mL Class A volumetric flask and dilute to the mark.

5.8 Mercuric nitrate titrant (0.141 N): Dissolve 24.2 g $Hg(NO_3)_2 \cdot H_2O$ in 900 mL of reagent water acidified with 5.0 mL concentrated HNO_3 in a 1 liter volumetric flask and dilute to the mark with reagent water. Filter, if necessary. Standardize against standard sodium chloride solution (Step 5.3) using the procedures outlined in Sec. 7.0. Adjust to exactly 0.141 N and check. Store in a dark bottle. A 1.00 mL aliquot is equivalent to 5.00 mg of chloride.

5.9 Mercuric nitrate titrant (0.025 N): Dissolve 4.2830 g $Hg(NO_3)_2 \cdot H_2O$ in 50 mL of reagent water acidified with 0.05 mL of concentrated HNO_3 (sp. gr. 1.42) in a 1 liter volumetric flask and dilute to the mark with reagent water. Filter, if necessary. Standardize against standard sodium chloride solution (Sec. 5.3) using the procedures outlined in Sec. 7.0. Adjust to exactly 0.025 N and check. Store in a dark bottle.

5.10 Mercuric nitrate titrant (0.0141 N): Dissolve 2.4200 g $Hg(NO_3)_2 \cdot H_2O$ in 25 mL of reagent water acidified with 0.25 mL of concentrated HNO_3 (sp. gr. 1.42) in a 1 liter Class A volumetric flask and dilute to the mark with reagent water. Filter, if necessary. Standardize against standard sodium chloride solution (Sec. 5.3) using the procedures outlined in Sec. 7.0. Adjust to exactly 0.0141 N and check. Store in a dark bottle. A 1 mL aliquot is equivalent to 500 μg of chloride.

5.11 Mixed indicator reagent: Dissolve 0.5 g crystalline diphenylcarbazone and 0.05 g bromophenol blue powder in 75 mL 95% ethanol in a 100 mL Class A volumetric flask and dilute to the mark with 95% ethanol. Store in brown bottle and discard after 6 months.

5.12 Alphazurine indicator solution: Dissolve 0.005 g of alphazurine blue-green dye in 95% ethanol or isopropanol in 100 mL Class A volumetric flask and dilute to the mark with 95% ethanol or isopropanol.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 There are no special requirements for preservation.

7.0 PROCEDURE

7.1 Place 50 mL of sample in a vessel for titration. If the concentration is greater than 20 mg/L chloride, use 0.141 N mercuric nitrate titrant (Sec. 5.8) in Sec. 7.6, or dilute sample with reagent water. If the concentration is less than 2.5 mg/L of chloride, use 0.0141 N mercuric nitrate titrant (Sec. 5.10) in Sec. 7.6. Using a 1 mL or 5 mL microburet, determine an indicator blank on 50 mL chloride-free water using Sec. 7.6. If the concentration is less than 0.1 mg/L of chloride, concentrate an appropriate volume to 50 mL.

7.2 Add 5 to 10 drops of mixed indicator reagent (Sec. 5.11); shake or swirl solution.

7.3 If a blue-violet or red color appears, add HNO_3 solution (Sec. 5.4) dropwise until the color changes to yellow. Proceed to Sec. 7.5.

7.4 If a yellow or orange color forms immediately on addition of the mixed indicator, add NaOH solution (Sec. 5.5) dropwise until the color changes to blue-violet; then add HNO_3 solution (Sec. 5.4) dropwise until the color changes to yellow.

7.5 Add 1 mL excess HNO_3 solution (Sec. 5.4).

7.6 Titrate with 0.025 N mercuric nitrate titrant (Sec. 5.9) until a blue-violet color persists throughout the solution. If volume of titrant exceeds 10 mL or is less than 1 mL, use the 0.141 N or 0.0141 N mercuric nitrate solutions, respectively. If necessary, take a small sample aliquot. Alphazurine indicator solution (Sec. 5.12) may be added with the indicator to sharpen the end point. This will change color shades. Practice runs should be made.

> Note: The use of indicator modifications and the presence of heavy metal ions can change solution colors without affecting the accuracy of the determination. For example, solutions containing alphazurine may be bright blue when neutral, grayish purple when basic, blue-green when acidic, and blue-violet at the chloride end point. Solutions containing about 100 mg/L nickel ion and normal mixed indicator are purple when neutral, green when acidic, and gray at the chloride end point. When applying this method to samples that contain colored ions or that require modified indicator, it is recommended that the operator become familiar with the specific color changes involved by experimenting with solutions prepared as standards for comparison of color effects.

7.6.1 If chromate is present at <100 mg/L and iron is not present, add 5-10 drops of alphazurine indicator solution (Sec. 5.12) and acidify to a pH of 3 (indicating paper). End point will then be an olive-purple color.

7.6.2 If chromate is present at >100 mg/L and iron is not present, add 2 mL of fresh hydroquinone solution (Sec. 5.7).

7.6.3 If ferric ion is present use a volume containing no more than 2.5 mg of ferric ion or ferric ion plus chromate ion. Add 2 mL fresh hydroquinone solution (Sec. 5.7).

7.6.4 If sulfite ion is present, add 0.5 mL of H_2O_2 solution (Sec. 5.6) to a 50 mL sample and mix for 1 min.

7.7 Calculation:

$$\text{mg chloride/liter} = \frac{(A - B)N \times 35{,}450}{\text{mL of sample}}$$

where:

A = mL titrant for sample;

B = mL titrant for blank; and

N = normality of mercuric nitrate titrant.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection. Refer to Chapter One for specific quality control guidelines.

8.2 Analyze a standard reference material to ensure that correct procedures are being followed and that all standard reagents have been prepared properly.

8.3 Employ a minimum of one blank per analytical batch or twenty samples, whichever is more frequent, to determine if contamination has occurred.

8.4 Run one matrix spike and matrix duplicate every analytical batch or twenty samples, whichever is more frequent. Matrix spikes and duplicates are brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

9.1 Water samples--A total of 42 analysts in 18 laboratories analyzed synthetic water samples containing exact increments of chloride, with the results shown in Table 1. In a single laboratory, using surface water samples at an average concentration of 34 mg Cl^-/L, the standard deviation was $\pm$1.0. A

synthetic unknown sample containing 241 mg/L chloride, 108 mg/L Ca, 82 mg/L Mg, 3.1 mg/L K, 19.9 mg/L Na, 1.1 mg/L nitrate N, 0.25 mg/L nitrate N, 259 mg/L sulfate and 42.5 mg/L total alkalinity (contributed by $NaHCO_3$) in reagent water was analyzed in 10 laboratories by the mercurimetric method, with a relative standard deviation of 3.3% and a relative error of 2.9%.

9.2 Oil combustates--These data are based on 34 data points obtained by five laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase oil in duplicate. The samples were combusted using Method 5050. A data point represents one duplicate analysis of a sample. One data point was judged to be an outlier and was not included in these results.

9.2.1 Precision and bias.

9.2.1.1 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 2):

$$Repeatability = 7.61\sqrt{x}*$$

*where x is the average of two results in μg/g.

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$Reproducibility = 20.02\sqrt{x}*$$

*where x is the average value of two results in μg/g.

9.2.1.2 Bias. The bias of this method varies with concentration, as shown in Table 3:

Bias = Amount found - Amount expected

10.0 REFERENCES

1. Annual Book of ASTM Standards, Part 31, "Water," Standard D512-67, Method A, p. 270 (1976).

2. Standard Methods for the Examination of Water and Wastewater, 15th ed., (1980).

3. U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020 (1983), Method 325.3.

TABLE 1. ANALYSES OF SYNTHETIC WATER SAMPLES FOR CHLORIDE BY MERCURIC NITRATE METHOD

Increment as Chloride (mg/L)	Precision as Standard Deviation (mg/L)	Accuracy as Bias (%)	Accuracy as Bias (mg/L)
17	1.54	+2.16	+0.4
18	1.32	+3.50	+0.6
91	2.92	+0.11	+0.1
97	3.16	-0.51	-0.5
382	11.70	-0.61	-2.3
398	11.80	-1.19	-4.7

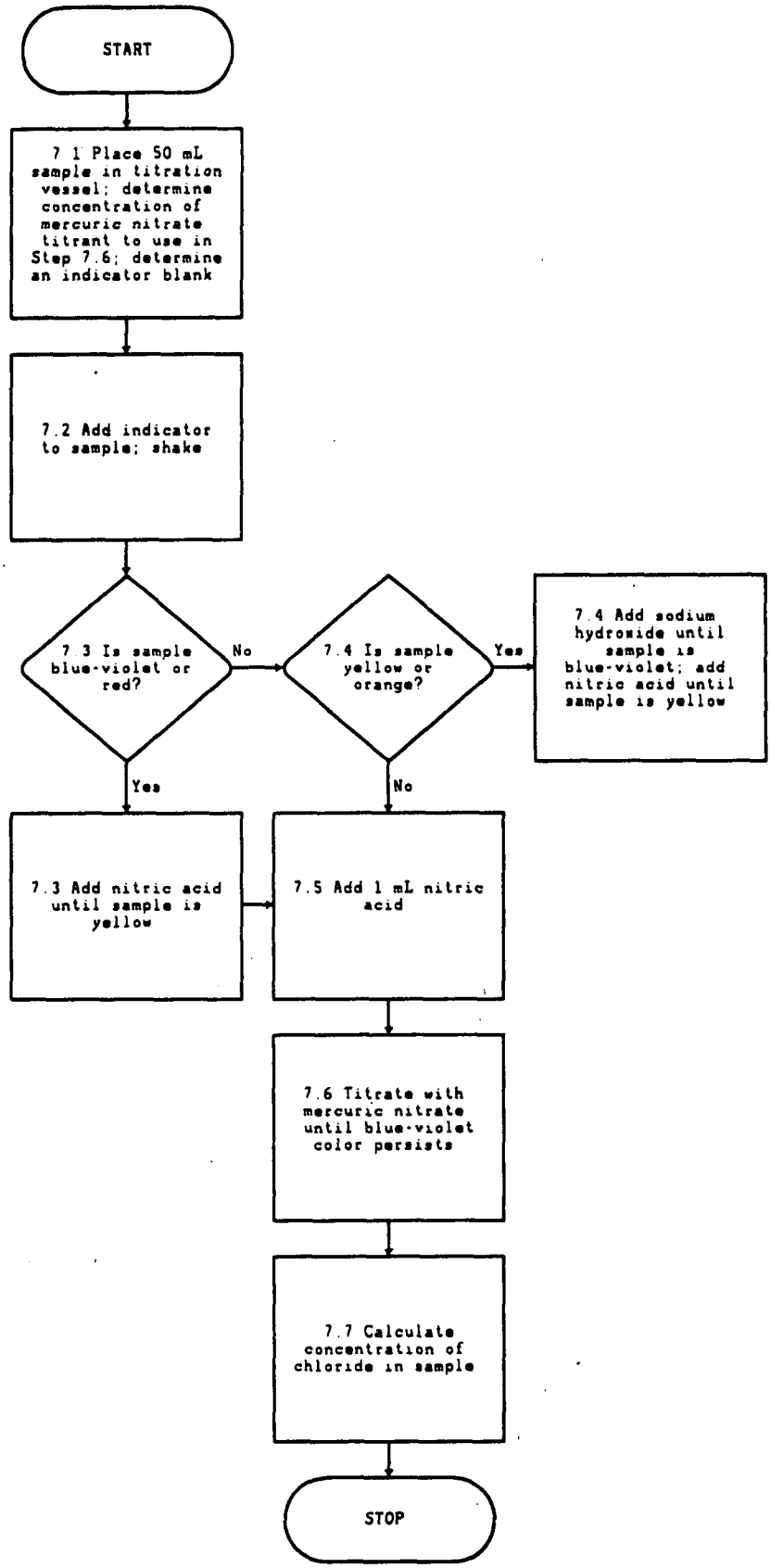
TABLE 2. REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND MERCURIC NITRATE TITRATION

Average value, µg/g	Repeatability, µg/g	Reproducibility, µg/g
500	170	448
1,000	241	633
1,500	295	775
2,000	340	895
2,500	381	1,001
3,000	417	1,097

TABLE 3. RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND MERCURIC NITRATE TITRATION

Amount expected, µg/g	Amount found, µg/g	Bias, µg/g	Percent bias
320	460	140	+44
480	578	98	+20
920	968	48	+ 5
1,498	1,664	166	+11
1,527	1,515	- 12	- 1
3,029	2,809	-220	- 7
3,045	2,710	-325	-11

METHOD 9252A
CHLORIDE (TITRIMETRIC, MERCURIC NITRATE)



METHOD 9253

CHLORIDE (TITRIMETRIC, SILVER NITRATE)

1.0 SCOPE AND APPLICATION

1.1 This method is intended primarily for oxygen bomb combustates or other waters where the chloride content is 5 mg/L or more and where interferences such as color or high concentrations of heavy metal ions render Method 9252 impracticable.

2.0 SUMMARY OF METHOD

2.1 Water adjusted to pH 8.3 is titrated with silver nitrate solution in the presence of potassium chromate indicator. The end point is indicated by persistence of the orange-silver chromate color.

3.0 INTERFERENCES

3.1 Bromide, iodide, and sulfide are titrated along with the chloride. Orthophosphate and polyphosphate interfere if present in concentrations greater than 250 and 25 mg/L, respectively. Sulfite and objectionable color or turbidity must be eliminated. Compounds that precipitate at pH 8.3 (certain hydroxides) may cause error by occlusion.

3.2 Residual sodium carbonate from the bomb combustion may react with silver nitrate to produce the precipitate, silver carbonate. This competitive reaction may interfere with the visual detection of the end point. To remove carbonate from the test solution, add small quantities of sulfuric acid followed by agitation.

4.0 APPARATUS AND MATERIALS

4.1 Standard laboratory titrimetric equipment, including 1 mL or 5 mL microburet with 0.01 mL gradations, and 25 mL buret.

4.2 Analytical balance: capable of weighing to 0.0001 g.

4.3 Class A volumetric flask: 1 L.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Hydrogen peroxide (30%), H_2O_2.

5.4 Phenolphthalein indicator solution (10 g/L).

5.5 Potassium chromate indicator solution. Dissolve 50 g of potassium chromate (K_2CrO_4) in 100 mL of reagent water and add silver nitrate ($AgNO_3$) until a slightly red precipitate is produced. Allow the solution to stand, protected from light, for at least 24 hours after the addition of $AgNO_3$. Then filter the solution to remove the precipitate and dilute to 1 L with reagent water.

5.6 Silver nitrate solution, standard (0.025N). Crush approximately 5 g of silver nitrate ($AgNO_3$) crystals and dry to constant weight at 40°C. Dissolve 4.2473 $\pm$ 0.0002 g of the crushed, dried crystals in reagent water and dilute to 1 L with reagent water. Standardize against the standard NaCl solution, using the procedure given in Section 7.0.

5.7 Sodium chloride solution, standard (0.025N). Dissolve 1.4613 g $\pm$ 0.0002 g of sodium chloride (dried at 600°C for 1 hr) in chloride-free water in a 1 liter Class A volumetric flask and dilute to the mark with reagent water.

5.8 Sodium hydroxide solution (0.25N). Dissolve approximately 10 g of NaOH in reagent water and dilute to 1 L with reagent water.

5.9 Sulfuric acid (1:19), H_2SO_4. Carefully add 1 volume of concentrated sulfuric acid to 19 volumes of reagent water, while mixing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 There are no special requirements for preservation.

7.0 PROCEDURE

7.1 Pour 50 mL or less of the sample, containing between 0.25 mg and 20 mg of chloride ion, into a white porcelain container. Dilute to approximately 50 mL with reagent water, if necessary. Adjust the pH to the phenolphthalein end point (pH 8.3) using H_2SO_4 (Sec. 5.9) or NaOH solution (Sec. 5.8).

7.2 Add approximately 1.0 mL of K_2CrO_4 indicator solution and mix. Add standard $AgNO_3$ solution dropwise from a 25 mL buret until the orange color persists throughout the sample when illuminated with a yellow light or viewed with yellow goggles. Be consistent with endpoint recognition.

7.3 Repeat the procedure described in Secs. 7.1 and 7.2 using exactly one-half as much original sample, diluted to 50 mL with halide-free water.

7.4 If sulfite ion is present, add 0.5 mL of H_2O_2 to the samples described in Secs. 7.2 and 7.3 and mix for 1 minute. Adjust the pH, then proceed as described in Secs. 7.2 and 7.3.

7.5 Calculation

7.5.1 Calculate the chloride ion concentration in the original sample, in milligrams per liter, as follows:

$$\text{Chloride (mg/L)} = [(V_1 - V_2) \times N \times 71{,}000] / S$$

where:

V_1 = Milliliters of standard $AgNO_3$ solution added in titrating the sample prepared in Sec. 7.1.

V_2 = Milliliters of standard $AgNO_3$ solution added in titrating the sample prepared in Sec. 7.3.

N = Normality of standard $AgNO_3$ solution.

S = Milliliters of original sample in the 50 mL test sample prepared in Sec. 7.1.

71,000 = 2 x 35,500 mg Cl^-/equivalent, since $V_1 \sim 2V_2$.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection. Refer to Chapter One for specific quality control guidelines.

8.2 Analyze a standard reference material to ensure that correct procedures are being followed and that all standard reagents have been prepared properly.

8.3 Employ a minimum of one blank per analytical batch or twenty samples, whichever is more frequent, to determine if contamination has occurred.

8.4 Run one matrix spike and matrix duplicate every analytical batch or twenty samples, whichever is more frequent. Matrix spikes and duplicates are brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

9.1 These data are based on 32 data points obtained by five laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. The samples were combusted using Method 5050. A data point represents one duplicate analysis of a sample. Three data points were judged to be outliers and were not included in these results.

9.1.1 Precision. The precision of the method as determined by the statistical examination of inter-laboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 1):

$$Repeatability = 0.36\ x^{*}$$

*where x is the average of two results in µg/g.

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$Reproducibility = 0.71\ x^{*}$$

*where x is the average of two results in µg/g.

9.1.2 Bias. The bias of this method varies with concentration, as shown in Table 2:

Bias = Amount found - Amount expected

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

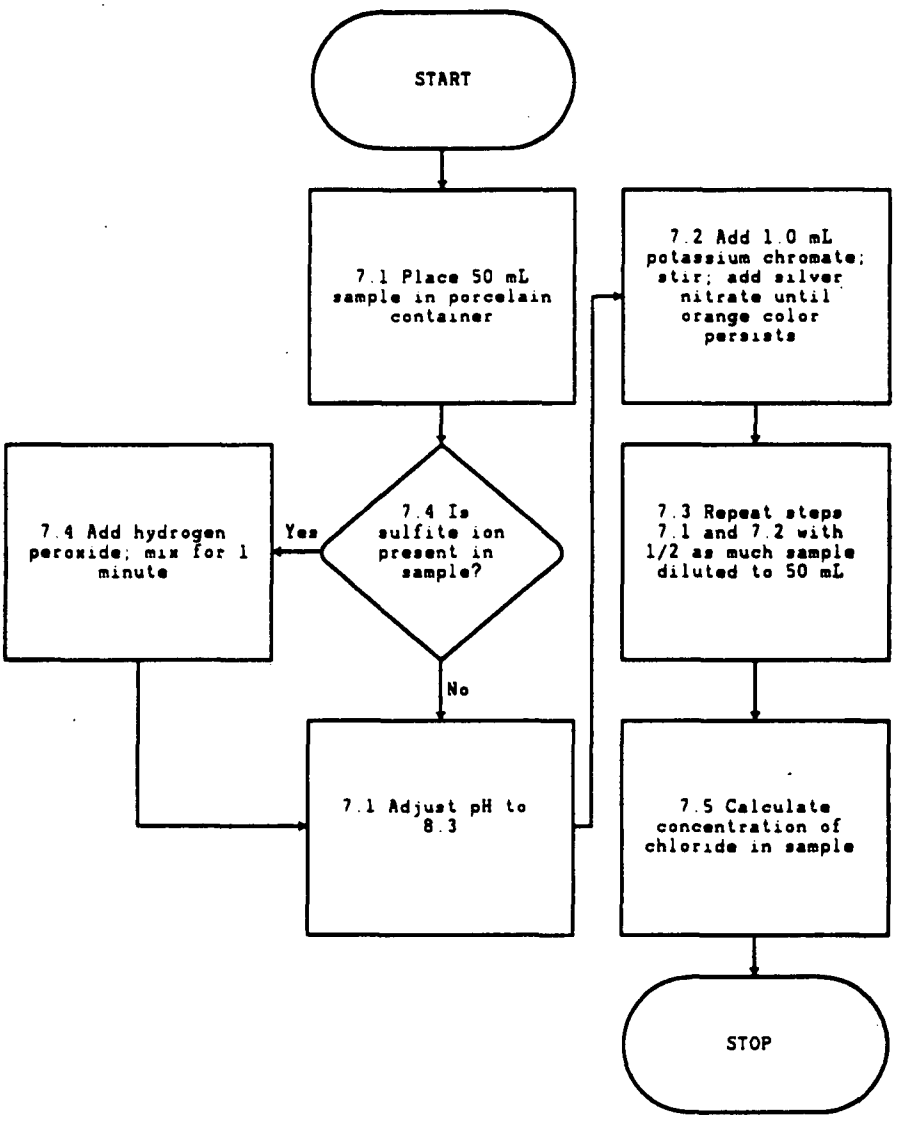
3. Gaskill, A.; Estes, E. D.; Hardison, D. L.; and Myers, L. E. "Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels," Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA 80. July 1988.

TABLE 1.
REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND SILVER NITRATE TITRATION

Average value (μg/g)	Repeatability (μg/g)	Reproducibility (μg/g)
500	180	355
1,000	360	710
1,500	540	1,065
2,000	720	1,420
2,500	900	1,775
3,000	1,080	2,130

TABLE 2.
RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND SILVER NITRATE TITRATION

Amount expected (μg/g)	Amount found (μg/g)	Bias, (μg/g)	Percent bias
320	645	325	+102
480	665	185	+39
920	855	-65	-7
1,498	1,515	17	+1
1,527	1,369	-158	-10
3,029	2,570	-460	-15
3,045	2,683	-362	-12


START
7.1 Place 50 mL sample in porcelain container
7.2 Add 1.0 mL potassium chromate; stir; add silver nitrate until orange color persists
7.4 Is sulfite ion present in sample?
Yes
7.4 Add hydrogen peroxide; mix for 1 minute
No
7.3 Repeat steps 7.1 and 7.2 with 1/2 as much sample diluted to 50 mL
7.1 Adjust pH to 8.3
7.5 Calculate concentration of chloride in sample
STOP

METHOD 9320

RADIUM-228

1.0 SCOPE AND APPLICATION

1.1 This method covers the measurement of radium-228 in ground water and, if desired, the determination of radium-226 on the same sample. If the level of radium-226 is above 3 pCi/L, the sample must also be measured for radium-228.

1.2 This technique is devised so that the beta activity from actinium-228, which is produced by decay of radium-228, can be determined and related to the radium-228 that is present in the sample.

1.3 To quantify actinium-228 and thus determine radium-228, the efficiency of the beta counter for measuring the very short half-lived actinium-228 (avg. beta energy of 0.404 keV) is to be calibrated with a beta source of comparable average beta energy.

2.0 SUMMARY OF METHOD

2.1 The radium in the water sample is collected by coprecipitation with barium and lead sulfate and purified by reprecipitation from EDTA solution. Both radium-226 and radium-228 are collected in this manner. After a 36-hr ingrowth of actinium-228 from radium-228, the actinium-228 is carried on yttrium oxalate, purified and beta counted. If radium-226 is also desired, the activity in the supernatant can be reserved for coprecipitation on barium sulfate, dissolving in EDTA and storing for ingrowth in a sealed radon bubbler.

3.0 INTERFERENCES

3.1 As evidenced by the results of the performance studies, the presence of strontium-90 in the water sample gives a positive bias to the radium-228 activity measured. However, strontium-90 is not likely to be found in ground water, except possibly in monitoring wells around a radioactive burial site.

3.2 Excess barium in the water sample might result in a falsely high chemical yield.

4.0 APPARATUS

4.1 Gas-flow proportional counting system (low-background beta <3 cpm).

4.2 Electric hot plate.

4.3 Centrifuge.

4.4 Membrane filters: Matricel 47-mm.

4.5 Drying lamp.

4.6 Glassware.

4.7 Stainless steel counting planchets.

4.8 Analytical balance.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water must be monitored for impurities.

5.2 Acetic acid, 17.4 N: Glacial CH_3COOH (concentrated) sp. gr. 1.05, 99.8%.

5.3 Ammonium hydroxide, 15 N: NH_4OH (concentrated) sp gr. 0.90, 56.6%.

5.4 Ammonium oxalate, 5%: Dissolve 5g $(NH_4)_2C_2O_4 \cdot H_2O$ in Type II water and dilute to 100 mL.

5.5 Ammonium sulfate, 200 mg/mL: Dissolve 20 g $(NH_4)_2SO_4$ in Type II water and dilute to 100 mL.

5.6 Ammonium sulfide, 2%: Dilute 10 mL $(NH_4)_2S$ (20-24%), to 100 mL with Type II water.

5.7 Barium carrier, 16 mg/mL, standardized: Dissolve 2.846 g $BaCl_2 \cdot 2H_2O$ in Type II water, add 0.5 mL 16 N HNO_3, and dilute to 100 mL with Type II water.

5.8 Citric acid, 1 M: Dissolve 19.2 g $C_6H_8O_7 \cdot H_2O$ in Type II water and dilute to 100 mL.

5.9 EDTA reagent, basic (0.25 M): Dissolve 20 g NaOH in 750 mL Type II water, heat, and slowly add 93 g disodium ethylenedinitriloacetate dihydrate ($Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$) while stirring. After the salt is in solution, filter through coarse filter paper, and dilute to 1 liter.

5.10 Lead carrier, 15 mg/mL: Dissolve 2.397 g $Pb(NO_3)_2$ in Type II water, add 0.5 mL 16 N HNO_3, and dilute to 100 mL with Type II water.

5.11 Lead carrier, 1.5 mg/mL: Dilute 10 mL lead carrier (15 mg/mL) to 100 mL with Type II water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected in a manner which addresses the considerations discussed in Chapter Nine of this manual.

6.2 It is recommended that samples be preserved at the time of collection by adding enough 1 N HNO_3 to the sample to bring it to pH 2 (15 mL 1 N HNO_3 per liter of sample is usually sufficient). If samples are to be collected without preservation, they should be brought to the laboratory within 5 days, then preserved, and held in the original container for a minimum of 16 hr before analysis or transfer of the sample. See also Note to Paragraph 7.2 below.

6.3 The container choice should be plastic (rather than glass) to prevent loss due to breakage during transportation and handling.

7.0 PROCEDURE

7.1 Calibrations:

7.1.1 **Counter efficiency:** The beta counter may be calibrated with actinium-228 or strontium-89 ($t_{1/2}$ = 51 d). Strontium-89 has an average beta energy of 0.589 KeV, while the average beta energy for actinium-228 is 0.404 KeV. A standard strontium-89 tracer solution can be used to determine beta efficiencies over a range of precipitate weights on the stainless steel planchet.

7.2 For each liter of water, add 5 mL 1 M $C_6H_8O_7 \cdot H_2O$, and a few drops of methyl orange indicator. The solution should be red.

NOTE: At the time of sample collection add 2 mL 16 N HNO_3 for each liter of water.

7.3 Add 10 mL lead carrier (15 mg/mL), 2 mL strontium carrier (10 mg/mL), 2.0 mL barium carrier (16 mg/mL), and 1 mL yttrium carrier (18 mg/mL); stir well. Add 15 N NH_4OH until a definite yellow color is obtained; then add a few drops excess. Heat to incipient boiling and maintain at this temperature for 30 min.

7.4 Precipitate lead and barium sulfates by adding 18 N H_2SO_4 until the red color reappears; then add 0.25 mL excess. Add 5 mL $(NH_4)_2SO_4$ (200 mg/mL) for each liter of sample. Stir frequently and keep at a temperature of about 90°C for 30 min.

7.5 Cool slightly; then filter with suction through a 47-mm matricel membrane filter (GA6,0.45-micron pore size). Make a quantitative transfer of precipitate to the filter by rinsing last particles out of beaker with a strong jet of water.

7.6 Carefully place filter with precipitate in the bottom of a 250-mL beaker. Add about 10 mL 16 N HNO_3 and heat gently until the filter completely

dissolves. Transfer the precipitate into a polypropylene centrifuge tube with additional 16 N HNO_3. Centrifuge and discard supernatant.

7.7 Wash the precipitate with 15 mL 16 N HNO_3, centrifuge, and discard supernatant. Repeat this washing a second time.

7.8 Add 25 mL basic EDTA reagent, heat in a hot-water bath, and stir well. Add a few drops 10 N NaOH if the precipitate does not readily dissolve.

7.9 Add 1 mL strontium-yttrium mixed carrier and stir thoroughly. Add a few drops 10 N NaOH if any precipitate forms.

7.10 Add 1 mL $(NH_4)_2SO_4$ (200 mg/mL) and stir thoroughly. Add 17.4 N acetic acid until barium sulfate precipitates; then add 2 mL excess. Digest in a hot water bath until precipitate settles. Centrifuge and discard supernatant.

7.11 Add 20 mL basic EDTA reagent, heat in a hot-water bath, and stir until precipitate dissolves. Repeat steps 7.9 and 7.10. (Note time of last barium sulfate precipitation; this is the beginning of the actinium-228 ingrowth time.)

7.12 Dissolve the precipitate in 20 mL basic EDTA reagent as before; then add 1.0 mL yttrium carrier (9 mg/mL) and 1 mL lead carrier (1.5 mg/mL). If any precipitate forms, dissolve by adding a few drops 10 N NaOH. Cap the polypropylene tube and age at least 36 hr.

7.13 Add 0.3 mL $(NH_4)_2S$ and stir well. Add 10 N NaOH dropwise with vigorous stirring until lead sulfide precipitates; then add 10 drops excess. Stir intermittently for about 10 min. Centrifuge and decant supernatant into a clean tube.

7.14 Add 1 mL lead carrier (1.5 mg/mL), 0.1 mL $(NH_4)_2S$, and a few drops 10 N NaOH. Repeat precipitation of lead sulfide as before. Centrifuge and filter supernate through Whatman #42 filter paper into a clean tube. Wash filter with a few mL water. Discard residue.

7.15 Add 5 mL 18 N NaOH, stir well, and digest in a hot-water bath until yttrium hydroxide coagulates. Centrifuge and decant supernate into a beaker. Save for barium yield determination (step 7.20). (Note time of yttrium hydroxide precipitation; this is the end of the actinium-228 ingrowth time and beginning of actinium-228 decay time.)

7.16 Dissolve the precipitate in 2 mL 6 N HNO_3. Heat and stir in a hot water bath about 5 min. Add 5 mL water and reprecipitate yttrium hydroxide with 3 mL 10 N NaOH. Heat and stir in a hot water bath until precipitate coagulates. Centrifuge and add this supernate to the supernate produced in step 7.15 in order to determine barium yield.

7.17 Dissolve precipitate with 1 mL 1 N HNO_3 and heat in hot-water bath a few minutes. Dilute to 5 mL and add 2 mL 5% $(NH_4)_2C_2O_4 \cdot H_2O$. Heat to coagulate, centrifuge, and discard supernatant.

7.18 Add 10 mL water, 6 drops 1 N HNO_3 and 6 drops 5% $(NH_4)_2C_2O_4 \cdot H_2O$. Heat and stir in a hot-water bath a few minutes. Centrifuge and discard supernatant.

7.19 To determine yttrium yield, transfer quantitatively to a tared stainless steel planchet with a minimum amount of water. Dry under an infrared lamp to a constant weight and count in a low-background beta counter.

7.20 To the supernatant from step 7.15, add 4 mL 16 N HNO_3 and 2 mL $(NH_4)_2SO_4$ (200 mg/mL), stirring well after each addition. Add 17.4 N acetic acid until barium sulfate precipitates; then add 2 mL excess. Digest on a hot plate until precipitate settles. Centrifuge and discard supernatant.

7.21 Add 20 mL basic EDTA reagent, rest in a hot-water bath, and stir until precipitate dissolves. Add a few drops 10 N NaOH if precipitate does not readily dissolve.

7.22 Add 1 mL $(NH_4)_2SO_4$ (200 mg/mL) and stir thoroughly. Add 17.4 N acetic acid until barium sulfate precipitates; then add 2 mL excess. Digest in a hot-water bath until precipitate settles. Centrifuge and discard supernatant.

7.23 Wash precipitate with 10 mL water. Centrifuge and discard supernatant.

7.24 Transfer precipitate to a tared stainless steel planchet with a minimum amount of water. Dry under an infrared lamp and weigh for barium yield determination.

7.25 Calculation:

7.25.1 Calculate the radium-228 concentration, D, in picocuries per liter as follows:

$$D = \frac{C}{2.22 \times EVR} \times \frac{\lambda t_2 \ *}{(1-e^{-\lambda t_2})} \times \frac{1}{(1-e^{-t_3})} \times \frac{1}{e^{-t_1}}$$

$* \ \frac{\lambda t_2}{(1-e^{-\lambda t_2})}$ is a factor to correct the average count rate to the count rate at the beginning of counting time.

where:

C = Average net count rate, cpm;

E = Counter efficiency, for actinium-228, or comparable beta energy nuclide;

V = Liters of sample used;

R = Fractional chemical yield of yttrium carrier (Step 7.19) multiplied by fractional chemical yield of barrier carrier (Step 7.24);

2.22 = Conversion factor from disintegrations/minute to picocuries;

λ = The decay constant for actinium-228 (0.001884 min^{-1});

t_1 = The time interval (in min) between the first yttrium hydroxide precipitation in Step 7.15 and the start of the counting time;

t_2 = The time interval of counting in min; and

t_3 = The ingrowth time of actinium-228 in min measured from the last barium sulfate precipitation in Step 7.11 to the first yttrium hydroxide precipitation in Step 7.15.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

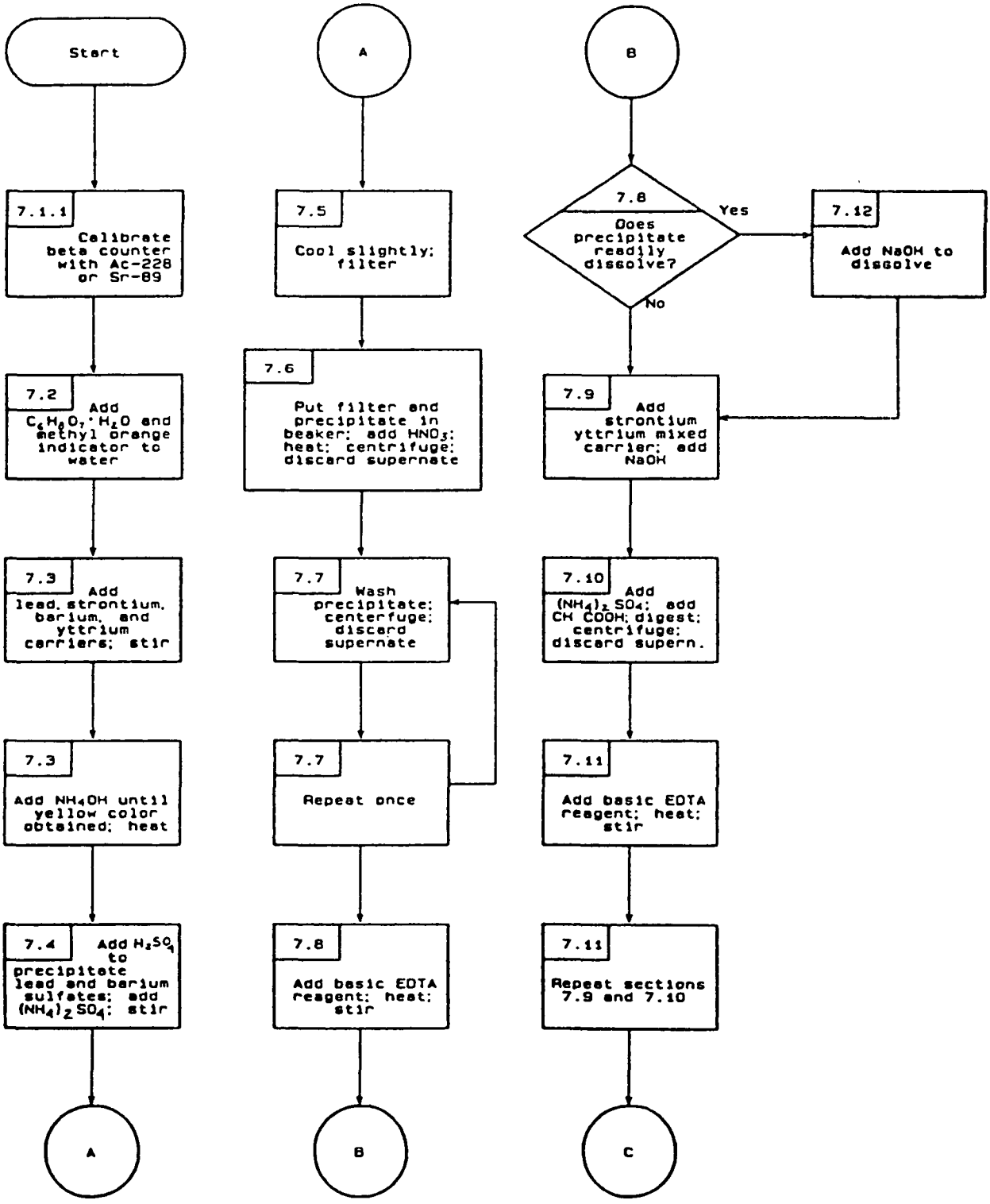
9.1 No data provided.

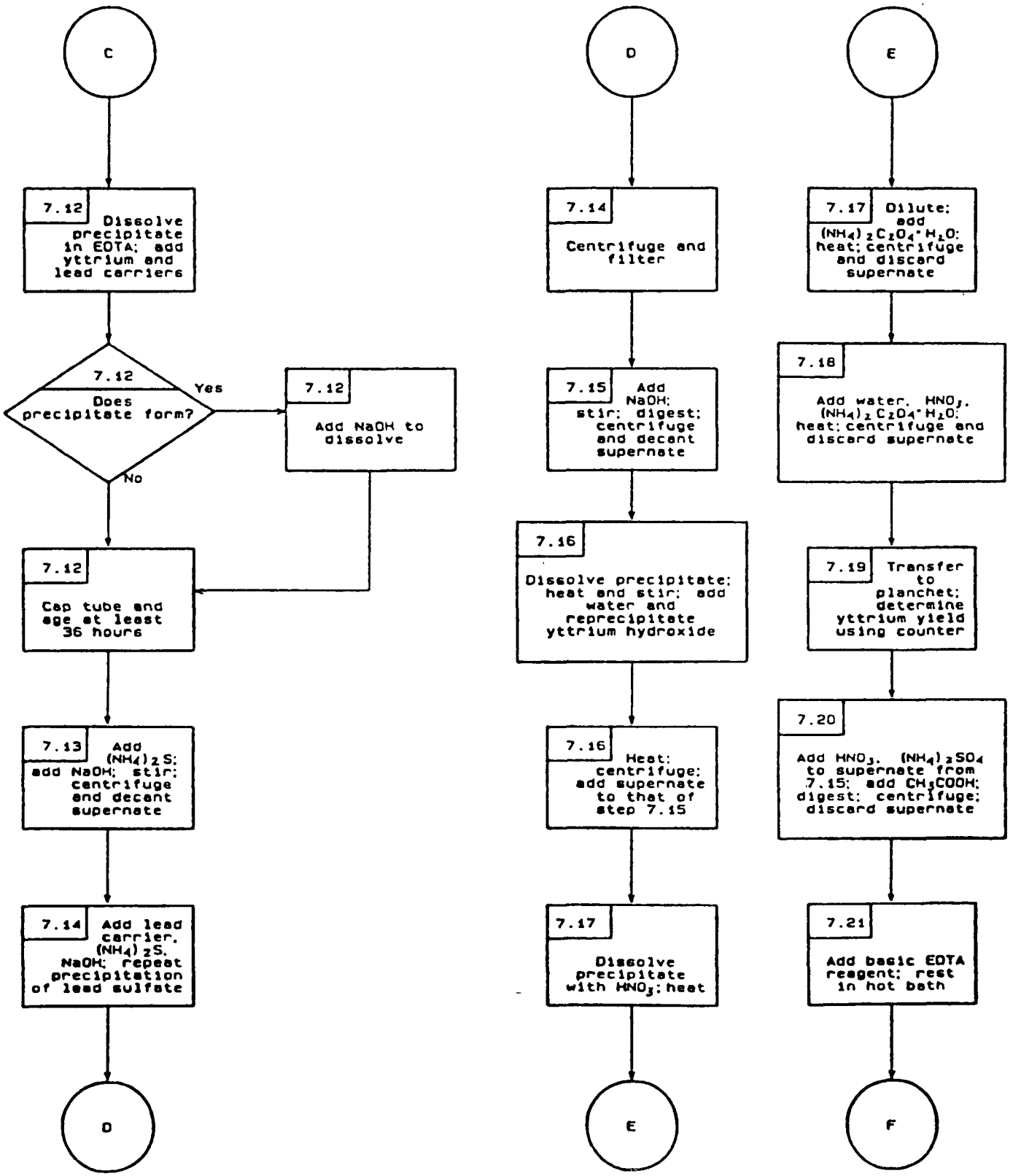
10.0 REFERENCES

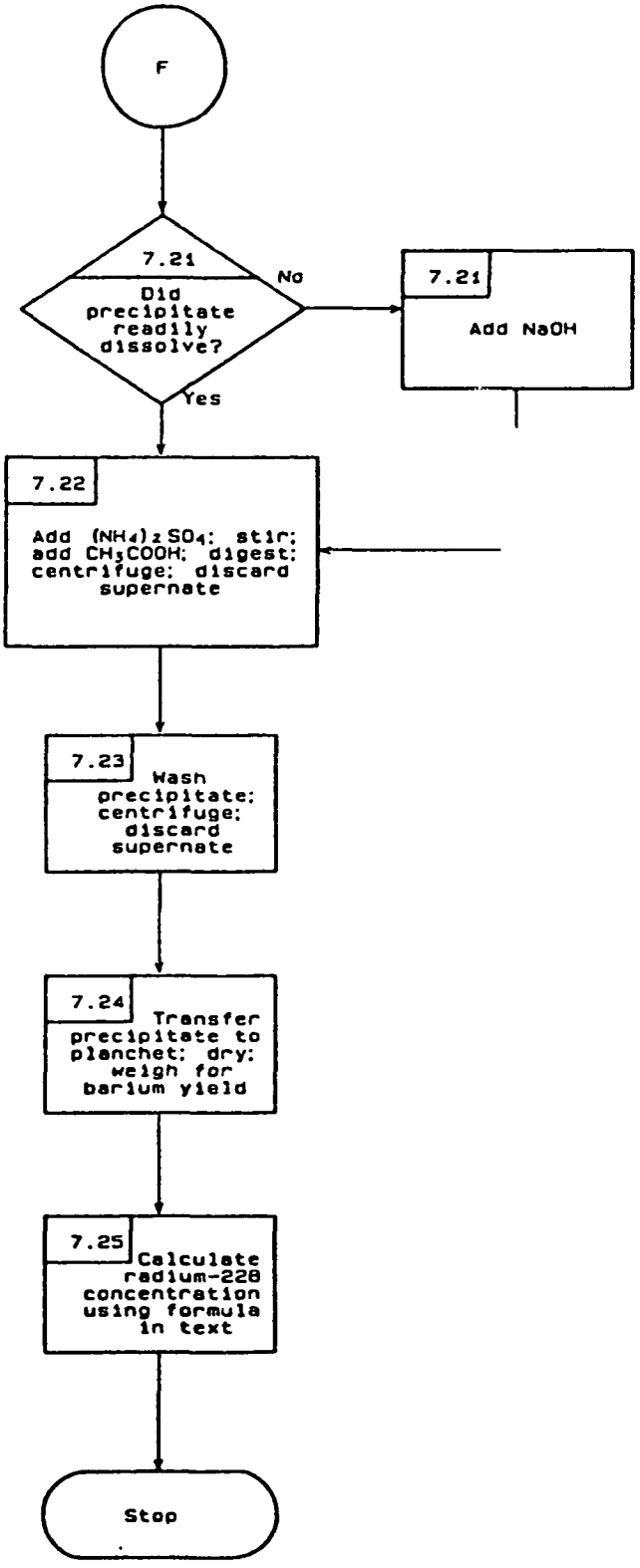
1. Greenberg, A.E., J.J. Connors, and D.J. Jenkens, eds., Standard Methods for the Examination of Water and Wastewater, 15th ed., American Public Health Assoc., Washington, D.C., Method 707, p. 600, 1980.

2. Johnson, J.O., Determination of Radium 228 in Natural Waters. Radiochemical Analysis of Water. U.S. Geol. Surv., Water Supply Paper 1696-G. U.S. Govt. Printing Office, Washington, D.C., 1971.

3. Krieger, H.L., Prescribed Procedures for Measurement of Radioactivity in Drinking Water, Environmental Monitoring and Support Laboratory, U.S. EPA, Cincinnati, OH, EPA-600/4-75-008, 1976.


Start
7.1.1 Calibrate beta counter with Ac-228 or Sr-89
7.2 Add $C_6H_8O_7 \cdot H_2O$ and methyl orange indicator to water
7.3 Add lead, strontium, barium, and yttrium carriers; stir
7.3 Add NH_4OH until yellow color obtained; heat
7.4 Add H_2SO_4 to precipitate lead and barium sulfates; add $(NH_4)_2SO_4$; stir
A
A
7.5 Cool slightly; filter
7.6 Put filter and precipitate in beaker; add HNO_3; heat; centrifuge; discard supernate
7.7 Wash precipitate; centerfuge; discard supernate
7.7 Repeat once
7.8 Add basic EDTA reagent; heat; stir
B
B
7.8 Does precipitate readily dissolve?
Yes
No
7.12 Add NaOH to dissolve
7.9 Add strontium yttrium mixed carrier; add NaOH
7.10 Add $(NH_4)_2SO_4$; add CH COOH; digest; centrifuge; discard supern.
7.11 Add basic EDTA reagent; heat; stir
7.11 Repeat sections 7.9 and 7.10
C


C
7.12 Dissolve precipitate in EDTA; add yttrium and lead carriers
7.12 Does precipitate form?
Yes
No
7.12 Add NaOH to dissolve
7.12 Cap tube and age at least 36 hours
7.13 Add $(NH_4)_2S$; add NaOH; stir; centrifuge and decant supernate
7.14 Add lead carrier, $(NH_4)_2S$, NaOH; repeat precipitation of lead sulfate
D
D
7.14 Centrifuge and filter
7.15 Add NaOH; stir; digest; centrifuge and decant supernate
7.16 Dissolve precipitate; heat and stir; add water and reprecipitate yttrium hydroxide
7.16 Heat; centrifuge; add supernate to that of step 7.15
7.17 Dissolve precipitate with HNO_3; heat
E
E
7.17 Dilute; add $(NH_4)_2C_2O_4 \cdot H_2O$; heat; centrifuge and discard supernate
7.18 Add water, HNO_3, $(NH_4)_2C_2O_4 \cdot H_2O$; heat; centrifuge and discard supernate
7.19 Transfer to planchet; determine yttrium yield using counter
7.20 Add HNO_3, $(NH_4)_2SO_4$ to supernate from 7.15; add CH_3COOH; digest; centrifuge; discard supernate
7.21 Add basic EDTA reagent; rest in hot bath
F


F
7.21
Did precipitate readily dissolve?
No
7.21
Add NaOH
Yes
7.22
Add $(NH_4)_2SO_4$; stir; add CH_3COOH; digest; centrifuge; discard supernate
7.23
Wash precipitate; centrifuge; discard supernate
7.24
Transfer precipitate to planchet; dry; weigh for barium yield
7.25
Calculate radium-228 concentration using formula in text
Stop

CHAPTER SIX

PROPERTIES

The following methods are found in Chapter Six:

Method 1312:	Synthetic Precipitation Leaching Procedure
Method 1320:	Multiple Extraction Procedure
Method 1330A:	Extraction Procedure for Oily Wastes
Method 9040A:	pH Electrometric Measurement
Method 9041A:	pH Paper Method
Method 9045B:	Soil and Waste pH
Method 9050:	Specific Conductance
Method 9080:	Cation-Exchange Capacity of Soils (Ammonium Acetate)
Method 9081:	Cation-Exchange Capacity of Soils (Sodium Acetate)
Method 9090A:	Compatibility Test for Wastes and Membrane Liners
Method 9095:	Paint Filter Liquids Test
Method 9096:	Liquid Release Test (LRT) Procedure
Method 9100:	Saturated Hydraulic Conductivity, Saturated Leachate Conductivity, and Intrinsic Permeability
Method 9310:	Gross Alpha and Gross Beta
Method 9315:	Alpha-Emitting Radium Isotopes

METHOD 1312

SYNTHETIC PRECIPITATION LEACHING PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 Method 1312 is designed to determine the mobility of both organic and inorganic analytes present in liquids, soils, and wastes.

2.0 SUMMARY OF METHOD

2.1 For liquid samples (i.e., those containing less than 0.5 % dry solid material), the sample, after filtration through a 0.6 to 0.8 μm glass fiber filter, is defined as the 1312 extract.

2.2 For samples containing greater than 0.5 % solids, the liquid phase, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the region of the country where the sample site is located if the sample is a soil. If the sample is a waste or wastewater, the extraction fluid employed is a pH 4.2 solution. A special extractor vessel is used when testing for volatile analytes (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fiber filter.

2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at 30 ± 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.2 Extraction Vessels

4.2.1 Zero Headspace Extraction Vessel (ZHE). This device is for use only when the sample is being tested for the mobility of volatile analytes (i.e., those listed in Table 1). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the

vessel (see Step 4.3.1). These vessels shall have an internal volume of 500-600 mL and be equipped to accommodate a 90-110 mm filter. The devices contain VITON®[1] O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psig or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for 1312 analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psig, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psig, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see Step 7.3) refers to pounds-per-square-inch (psig), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

4.2.2 Bottle Extraction Vessel. When the sample is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see Step 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Step 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.3 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.3.1 Zero-Headspace Extraction Vessel (ZHE): When the sample is evaluated for volatiles, the zero-headspace extraction vessel described in Step 4.2.1 is used for filtration. The device shall be capable of

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[1]VITON® is a trademark of Du Pont.

supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psig).

NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.3.2 Filter Holder: When the sample is evaluated for other than volatile analytes, a filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psig or more. The type of filter holder used depends on the properties of the material to be filtered (see Step 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10 %) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are listed in Table 4.

4.3.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb sample components of interest. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high-density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used only when evaluating the mobility of metals. Borosilicate glass bottles are recommended for use over other types of glass bottles, especially when inorganics are analytes of concern.

4.4 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8-μm . Filters known to EPA which meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with reagent water (a minimum of 1-L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters: The meter should be accurate to $\pm$ 0.05 units at 25°C.

4.6 ZHE Extract Collection Devices: TEDLAR®[2] bags or glass, stainless steel or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract when using the ZHE device. These devices listed are recommended for use under the following conditions:

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., <1 % of

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[2]TEDLAR® is a registered trademark of Du Pont.

total waste), the TEDLAR® bag or a 600 mL syringe should be used to collect and combine the initial liquid and solid extract.

4.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., >1 % of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100 % solid) or has no significant solid phase (is <0.5% solid) , either the TEDLAR® bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g., a positive displacement or peristaltic pump, a gas-tight syringe, pressure filtration unit (see Step 4.3.2), or other ZHE device).

4.8 Laboratory Balance: Any laboratory balance accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.1 grams).

4.9 Beaker or Erlenmeyer flask, glass, 500 mL.

4.10 Watchglass, appropriate diameter to cover beaker or Erlenmeyer flask.

4.11 Magnetic stirrer.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analyte(s) of interest. For nonvolatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.2.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 grams of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.2.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.2.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 ± 5 degrees C, bubble a contaminant-free inert gas (e.g. nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-headspace and seal with a Teflon-lined septum and cap.

5.3 Sulfuric acid/nitric acid (60/40 weight percent mixture) H_2SO_4/HNO_3. Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid. If preferred, a more dilute H_2SO_4/HNO_3 acid mixture may be prepared and used in steps 5.4.1 and 5.4.2 making it easier to adjust the pH of the extraction fluids.

5.4 Extraction fluids.

5.4.1 Extraction fluid #1: This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids (or a suitable dilution) to reagent water (Step 5.2) until the pH is 4.20 ± 0.05. The fluid is used to determine the leachability of soil from a site that is east of the Mississippi River, and the leachability of wastes and wastewaters.

NOTE: Solutions are unbuffered and exact pH may not be attained.

5.4.2 Extraction fluid #2: This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids (or a suitable dilution) to reagent water (Step 5.2) until the pH is 5.00 ± 0.05. The fluid is used to determine the leachability of soil from a site that is west of the Mississippi River.

5.4.3 Extraction fluid #3: This fluid is reagent water (Step 5.2) and is used to determine cyanide and volatiles leachability.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.5 Analytical standards shall be prepared according to the appropriate analytical method.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples shall be collected using an appropriate sampling plan.

6.2 There may be requirements on the minimal size of the field sample depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for the preliminary evaluations of the percent

solids and the particle size. An aliquot may be needed to conduct the nonvolatile analyte extraction procedure. If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more sample just in case something goes wrong with the initial attempt to conduct the test.

6.3 Preservatives shall not be added to samples before extraction.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the sample is to be evaluated for volatile analytes, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4°C. Samples should be opened only immediately prior to extraction).

6.6 1312 extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs (see Step 7.2.14 if precipitation occurs). Extracts should be preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See Step 8.0 (Quality Control) for acceptable sample and extract holding times.

7.0 PROCEDURE

7.1 Preliminary Evaluations

Perform preliminary 1312 evaluations on a minimum 100 gram aliquot of sample. This aliquot may not actually undergo 1312 extraction. These preliminary evaluations include: (1) determination of the percent solids (Step 7.1.1); (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (Step 7.1.2); and (3) determination of whether the solid portion of the waste requires particle size reduction (Step 7.1.3).

7.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1.1 If the sample will obviously yield no free liquid when subjected to pressure filtration (i.e., is 100% solid), weigh out a representative subsample (100 g minimum) and proceed to Step 7.1.3.

7.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device

discussed in Step 4.3.2, and is outlined in Steps 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.1.4 Assemble filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.1.6 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.1.7 Quantitatively transfer the sample to the filter holder (liquid and solid phases). Spread the sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

Gradually apply vacuum or gentle pressure of 1-10 psig, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psig, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10 psig increments to a maximum of 50 psig. After each incremental increase of 10 psig, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psig increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psig (i.e., filtration does not result in any additional filtrate within any 2-minute period), stop the filtration.

NOTE: If sample material (>1 % of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.1.1.5 to determine the weight of the sample that will be filtered.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.1.8 The material in the filter holder is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase.

NOTE: Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid, but even after applying vacuum or pressure filtration, as outlined in Step 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Step 7.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the sample by subtracting the weight of the liquid phase from the weight of the total sample, as determined in Step 7.1.1.5 or 7.1.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (Step 7.1.1.9)}}{\text{Total weight of waste (Step 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2 If the percent solids determined in Step 7.1.1.9 is equal to or greater than 0.5%, then proceed either to Step 7.1.3 to determine whether the solid material requires particle size reduction or to Step 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in Step 7.1.1.9 is less than 0.5%, then proceed to Step 7.2.9 if the nonvolatile 1312 analysis is to be performed, and to Step 7.3 with a fresh portion of the waste if the volatile 1312 analysis is to be performed.

7.1.2.1 Remove the solid phase and filter from the filtration apparatus.

7.1.2.2 Dry the filter and solid phase at 100 $\pm$ 20°C until two successive weighings yield the same value within $\pm$ 1 %. Record the final weight.

Caution: The drying oven should be vented to a hood or other appropriate device to eliminate the possibility of fumes from the sample escaping into the laboratory. Care should be taken to ensure that the sample will not flash or violently react upon heating.

7.1.2.3 Calculate the percent dry solids as follows:

$$\text{Percent dry solids} = \frac{\text{(Weight of dry sample + filter) - tared weight of filter}}{\text{Initial weight of sample (Step 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5%, then proceed to Step 7.2.9 if the nonvolatile 1312 analysis is to be performed, and to Step 7.3 if the volatile 1312 analysis is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile 1312 analysis is to be performed, return to the beginning of this Step (7.1) and, with a fresh portion of sample, determine whether particle size reduction is necessary (Step 7.1.3).

7.1.3 Determination of whether the sample requires particle-size reduction (particle-size is reduced during this step): Using the solid portion of the sample, evaluate the solid for particle size. Particle-size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see Step 7.3.6).

NOTE: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample-specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

7.1.4 Determination of appropriate extraction fluid:

7.1.4.1 For soils, if the sample is from a site that is east of the Mississippi River, extraction fluid #1 should be used. If the sample is from a site that is west of the Mississippi River, extraction fluid #2 should be used.

7.1.4.2 For wastes and wastewater, extraction fluid #1 should be used.

7.1.4.3 For cyanide-containing wastes and/or soils, extraction fluid #3 (reagent water) must be used because leaching of cyanide-containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

7.1.5 If the aliquot of the sample used for the preliminary evaluation (Steps 7.1.1 - 7.1.4) was determined to be 100% solid at Step 7.1.1.1, then it can be used for the Step 7.2 extraction (assuming at least 100 grams remain), and the Step 7.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in Step 7.1.1.7, then another aliquot shall be used for the volatile extraction procedure in Step 7.3. The aliquot of the waste subjected to the procedure in Step 7.1.1.7 might be appropriate for use for the Step 7.2 extraction if an adequate amount of solid (as determined by Step 7.1.1.9)

was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to Step 7.2.10 of the nonvolatile 1312 extraction.

7.2 Procedure When Volatiles Are Not Involved

A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample (percent solids, See Step 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of 1312 extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single 1312 extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the sample will obviously yield no liquid when subjected to pressure filtration (i.e., is 100 % solid, see Step 7.1.1), weigh out a subsample of the sample (100 gram minimum) and proceed to Step 7.2.9.

7.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in Step 4.3.2 and is outlined in Steps 7.2.3 to 7.2.8.

7.2.3 Pre-weigh the container that will receive the filtrate.

7.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Step 4.4).

NOTE: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.

7.2.5 Weigh out a subsample of the sample (100 gram minimum) and record the weight. If the waste contains <0.5 % dry solids (Step 7.1.2), the liquid portion of the waste, after filtration, is defined as the 1312 extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the 1312 extract. For wastes containing >0.5 % dry solids (Steps 7.1.1 or 7.1.2), use the percent solids information obtained in Step 7.1.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the 1312 extract.

7.2.6 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the sample is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.2.7 Quantitatively transfer the sample (liquid and solid phases) to the filter holder (see Step 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

Gradually apply vacuum or gentle pressure of 1-10 psig, until air or pressurizing gas moves through the filter. If this point if not reached under 10 psig, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10-psig increments to maximum of 50 psig. After each incremental increase of 10 psig, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psig increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psig (i.e., filtration does not result in any additional filtrate within a 2-minute period), stop the filtration.

NOTE: If waste material (>1 % of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.2.5, to determine the weight of the waste sample that will be filtered.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.2.8 The material in the filter holder is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (see Step 7.2.12) or stored at 4°C until time of analysis.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material which appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Step 7.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.2.9 If the sample contains <0.5% dry solids (see Step 7.1.2), proceed to Step 7.2.13. If the sample contains >0.5 % dry solids (see Step 7.1.1 or 7.1.2), and if particle-size reduction of the solid was needed in Step 7.1.3, proceed to Step 7.2.10. If the sample as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Step 7.2.11.

7.2.10 Prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a surface area or particle-size as described in Step 7.1.3. When the surface area or particle-size has been appropriately altered, quantitatively transfer the solid material

into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon-coated sieve should be used to avoid contamination of the sample.

7.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \%\ \text{solids (Step 7.1.1)} \times \text{weight of waste filtered (Step 7.2.5 or 7.2.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Step 7.1.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary extractor device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ± 2°C during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of sample (e.g., limed or calcium carbonate-containing sample may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

7.2.12 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Step 7.2.7. For final filtration of the 1312 extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed (see Step 4.4) if evaluating the mobility of metals.

7.2.13 Prepare the 1312 extract as follows:

7.2.13.1 If the sample contained no initial liquid phase, the filtered liquid material obtained from Step 7.2.12 is defined as the 1312 extract. Proceed to Step 7.2.14.

7.2.13.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from Step 7.2.12 with the initial liquid phase of the sample obtained in Step 7.2.7. This combined liquid is defined as the 1312 extract. Proceed to Step 7.2.14.

7.2.13.3 If the initial liquid phase of the waste, as obtained from Step 7.2.7, is not or may not be compatible with the filtered liquid resulting from Step 7.2.12, do not combine these

liquids. Analyze these liquids, collectively defined as the 1312 extract, and combine the results mathematically, as described in Step 7.2.14.

7.2.14 Following collection of the 1312 extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to pH < 2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4°C) until analyzed. The 1312 extract shall be prepared and analyzed according to appropriate analytical methods. 1312 extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to $\pm$ 0.5 %), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)\ (C_1) + (V_2)\ (C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.2.15 Compare the analyte concentrations in the 1312 extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

7.3 Procedure When Volatiles Are Involved

Use the ZHE device to obtain 1312 extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of non-volatile analytes (e.g., metals, pesticides, etc.).

The ZHE device has approximately a 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a sample from which no additional liquid may be forced out by an applied pressure of 50 psig), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the sample, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4°C) to minimize loss of volatiles.

7.3.1 Pre-weigh the (evacuated) filtrate collection container (see Step 4.6) and set aside. If using a TEDLAR® bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis. The containers listed in Step 4.6 are recommended for use under the conditions stated in Steps 4.6.1-4.6.3.

7.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Step 7.3, Step 7.1.1 and/or 7.1.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

7.3.3 If the sample is 100% solid (see Step 7.1.1), weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to Step 7.3.5.

7.3.4 If the sample contains <0.5% dry solids (Step 7.1.2), the liquid portion of waste, after filtration, is defined as the 1312 extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For samples containing $\geq$0.5% dry solids (Steps 7.1.1 and/or 7.1.2), use the percent solids information obtained in Step 7.1.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows:

7.3.4.1 For samples containing <5% solids (see Step 7.1.1), weigh out a 500 gram subsample of waste and record the weight.

7.3.4.2 For wastes containing >5% solids (see Step 7.1.1), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{percent solids (Step 7.1.1)}} \times 100$$

Weigh out a subsample of the waste of the appropriate size and record the weight.

7.3.5 If particle-size reduction of the solid portion of the sample was required in Step 7.1.3, proceed to Step 7.3.6. If particle-size reduction was not required in Step 7.1.3, proceed to Step 7.3.7.

7.3.6 Prepare the sample for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle size as described in Step 7.1.3.1. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4°C prior to particle-size reduction. The means used to effect particle-size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

> NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle-size has been appropriately altered, proceed to Step 7.3.7.

7.3.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge samples prior to filtration.

7.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens into the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extraction collection device to the top plate.

> Note: If sample material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Step 7.3.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psig (or more if necessary) to force all headspace slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100 % solid (see Step 7.1.1), slowly increase the pressure to a maximum of 50 psig to force most of the headspace out of the device and proceed to Step 7.3.12.

7.3.9 Attach the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psig to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10-psig increments to a maximum of 50 psig. After each incremental increase of 10 psig, if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psig increment. When liquid flow has ceased such that continued pressure filtration at 50 psig does not result in any additional filtrate within a 2-minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.3.10 The material in the ZHE is defined as the solid phase of the sample and the filtrate is defined as the liquid phase.

NOTE: Some samples, such as oily wastes and some paint wastes, will obviously contain some material which appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the 1312 extraction as a solid.

If the original waste contained <0.5 % dry solids (see Step 7.1.2), this filtrate is defined as the 1312 extract and is analyzed directly. Proceed to Step 7.3.15.

7.3.11 The liquid phase may now be either analyzed immediately (see Steps 7.3.13 through 7.3.15) or stored at 4°C under minimal headspace conditions until time of analysis. Determine the weight of extraction fluid #3 to add to the ZHE as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \%\ \text{solids (Step 7.1.1)} \times \text{weight of waste filtered (Step 7.3.4 or 7.3.8)}}{100}$$

7.3.12 The following steps detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #3 is used in all cases (see Step 5.4.3).

7.3.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into

the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

7.3.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psig (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psig and check all ZHE fittings to ensure that they are closed.

7.3.12.3 Place the ZHE in the rotary extractor apparatus (if it is not already there) and rotate at 30 $\pm$ 2 rpm for 18 $\pm$ 2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 23 $\pm$ 2°C during agitation.

7.3.13 Following the 18 $\pm$ 2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the ZHE is leaking. Check the ZHE for leaking as specified in Step 4.2.1, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Step 7.3.9. All extracts shall be filtered and collected if the TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (see Steps 4.6 and 7.3.1).

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured

7.3.14 If the original sample contained no initial liquid phase, the filtered liquid material obtained from Step 7.3.13 is defined as the 1312 extract. If the sample contained an initial liquid phase, the filtered liquid material obtained from Step 7.3.13 and the initial liquid phase (Step 7.3.9) are collectively defined as the 1312 extract.

7.3.15 Following collection of the 1312 extract, immediately prepare the extract for analysis and store with minimal headspace at 4°C

until analyzed. Analyze the 1312 extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume- weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)\ (C_1) + (V_2)\ (C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phases (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.3.16 Compare the analyte concentrations in the 1312 extract with the levels identified in the appropriate regulations. Refer to Step 8.0 for quality assurance requirements.

8.0 QUALITY CONTROL

8.1 A minimum of one blank (using the same extraction fluid as used for the samples) for every 20 extractions that have been conducted in an extraction vessel. Refer to Chapter One for additional quality control protocols.

8.2 A matrix spike shall be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data is being used solely to demonstrate that the waste property exceeds the regulatory level. A minimum of one matrix spike must be analyzed for each analytical batch. As a minimum, follow the matrix spike addition guidance provided in each analytical method.

8.2.1 Matrix spikes are to be added after filtration of the 1312 extract and before preservation. Matrix spikes should not be added prior to 1312 extraction of the sample.

8.2.2 In most cases, matrix spike levels should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration, but may not be less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of 1312 extract as that which was analyzed for the unspiked sample.

8.2.3 The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether

matrix interferences exist. Use of other internal calibration methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the analyte concentration in the 1312 extract when the recovery of the matrix spike is below the expected analytical method performance.

8.2.4 Matrix spike recoveries are calculated by the following formula:

$$\%R\ (\%\ \text{Recovery}) = 100\ (X_s - X_u) / K$$

where:

X_s = measured value for the spiked sample
X_u = measured value for the unspiked sample, and
K = known value of the spike in the sample.

8.3 All quality control measures described in the appropriate analytical methods shall be followed.

8.4 The use of internal calibration quantitation methods shall be employed for a metallic contaminant if: (1) Recovery of the contaminant from the 1312 extract is not at least 50% and the concentration does not exceed the appropriate regulatory level, and (2) The concentration of the contaminant measured in the extract is within 20% of the appropriate regulatory level.

8.4.1. The method of standard additions shall be employed as the internal calibration quantitation method for each metallic contaminant.

8.4.2 The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution. It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots. The forth aliquot is the unknown. Preferably, the first addition should be prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100% and 150% of the expected concentration of the sample. All four aliquots are maintained at the same final volume by adding reagent water or a blank solution, and may need dilution adjustment to maintain the signals in the linear range of the instrument technique. All four aliquots are analyzed.

8.4.3 Prepare a plot, or subject data to linear regression, of instrument signals or external-calibration-derived concentrations as the dependant variable (y-axis) versus concentrations of the additions of standards as the independent variable (x-axis). Solve for the intercept of the abscissa (the independent variable, x-axis) which is the concentration in the unknown.

8.4.4 Alternately, subtract the instrumental signal or external-calibration-derived concentration of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions. Plot or subject to linear regression of the corrected instrument signals or external-calibration-derived concentra-

tions as the dependant variable versus the independent variable. Derive concentrations for the unknowns using the internal calibration curve as if it were an external calibration curve.

8.5 Samples must undergo 1312 extraction within the following time periods:

SAMPLE MAXIMUM HOLDING TIMES (days)

	From: Field Collection To: 1312 extraction	From: 1312 extraction To: Preparative extraction	From: Preparative extraction To: Determinative analysis	Total Elapsed Time
Volatiles	14	NA	14	28
Semi-volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360
NA = Not Applicable				

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

9.0 METHOD PERFORMANCE

9.1 Precision results for semi-volatiles and metals: An eastern soil with high organic content and a western soil with low organic content were used for the semi-volatile and metal leaching experiments. Both types of soil were analyzed prior to contaminant spiking. The results are shown in Table 6. The concentration of contaminants leached from the soils were reproducible, as shown by the moderate relative standard deviations (RSDs) of the recoveries (averaging 29% for the compounds and elements analyzed).

9.2 Precision results for volatiles: Four different soils were spiked and tested for the extraction of volatiles. Soils One and Two were from western and eastern Superfund sites. Soils Three and Four were mixtures of a western soil with low organic content and two different municipal sludges. The results are shown in Table 7. Extract concentrations of volatile organics from the eastern soil were lower than from the western soil. Replicate leachings of Soils

Three and Four showed lower precision than the leachates from the Superfund soils.

10.0 REFERENCES

1. Environmental Monitoring Systems Laboratory, "Performance Testing of Method 1312; QA Support for RCRA Testing: Project Report". EPA/600/4-89/022. EPA Contract 68-03-3249 to Lockheed Engineering and Sciences Company, June 1989.

2. Research Triangle Institute, "Interlaboratory Comparison of Methods 1310, 1311, and 1312 for Lead in Soil". U.S. EPA Contract 68-01-7075, November 1988.

Table 1. Volatile Analytes[1]

Compound	CAS No.
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1,-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[1] When testing for any or all of these analytes, the zero-headspace extractor vessel shall be used instead of the bottle extractor.

Table 2. Suitable Rotary Agitation Apparatus[1]

Company	Location	Model No.
Analytical Testing and Consulting Services, Inc.	Warrington, PA (215) 343-4490	4-vessel extractor (DC20S); 8-vessel extractor (DC20); 12-vessel extractor (DC20B)
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	2-vessel (3740-2); 4-vessel (3740-4); 6-vessel (3740-6); 8-vessel (3740-8); 12-vessel (3740-12); 24-vessel (3740-24)
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	8-vessel (08-00-00) 4-vessel (04-00-00)
IRA Machine Shop and Laboratory	Santurce, PR (809) 752-4004	8-vessel (011001)
Lars Lande Manufacturing	Whitmore Lake, MI (313) 449-4116	10-vessel (10VRE) 5-vessel (5VRE)
Millipore Corp.	Bedford, MA (800) 225-3384	4-ZHE or 4 1-liter bottle extractor (YT300RAHW)

[1] Any device that rotates the extraction vessel in an end-over-end fashion at 30 ±2 rpm is acceptable.

Table 3. Suitable Zero-Headspace Extractor Vessels[1]

Company	Location	Model No.
Analytical Testing & Consulting Services, Inc.	Warrington, PA (215) 343-4490	C102, Mechanical Pressure Device
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	3745-ZHE, Gas Pressure Device
Lars Lande Manufacturing[2]	Whitmore Lake, MI (313) 449-4116	ZHE-11, Gas Pressure Device
Millipore Corporation	Bedford, MA (800) 225-3384	YT30090HW, Gas Pressure Device
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	VOLA-TOX1, Gas Pressure Device

[1] Any device that meets the specifications listed in Step 4.2.1 of the method is suitable.

[2] This device uses a 110 mm filter.

Table 4. Suitable Filter Holders[1]

Company	Location	Model/ Catalogue #	Size
Nucleopore Corporation	Pleasanton, CA (800) 882-7711	425910 410400	142 mm 47 mm
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	302400 311400	142 mm 47 mm
Millipore Corporation	Bedford, MA (800) 225-3384	YT30142HW XX1004700	142 mm 47 mm

[1] Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic analytes are of concern. The 142 mm size filter holder is recommended.

Table 5. Suitable Filter Media[1]

Company	Location	Model	Pore Size (μm)
Millipore Corporation	Bedford, MA (800) 225-3384	AP40	0.7
Nucleopore Corporation	Pleasanton, CA (415) 463-2530	211625	0.7
Whatman Laboratory Products, Inc.	Clifton, NJ (201) 773-5800	GFF	0.7
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	GF75	0.7

[1] Any filter that meets the specifications in Step 4.4 of the Method is suitable.

TABLE 6 - METHOD 1312 PRECISION RESULTS FOR SEMI-VOLATILES AND METALS

		Eastern Soil (pH 4.2)		Western Soil (pH 5.0)	
	Amount Spiked (µg)	Amount Recovered* (µg)	% RSD	Amount Recovered* (µg)	% RSD
FORTIFIED ANALYTES					
bis(2-chloroethyl)-ether	1040	834	12.5	616	14.2
2-Chlorophenol	1620	1010	6.8	525	54.9
1,4-Dichlorobenzene	2000	344	12.3	272	34.6
1,2-Dichlorobenzene	8920	1010	8.0	1520	28.4
2-Methylphenol	3940	1860	7.7	1130	32.6
Nitrobenzene	1010	812	10.0	457	21.3
2,4-Dimethylphenol	1460	200	18.4	18	87.6
Hexachlorobutadiene	6300	95	12.9	280	22.8
Acenaphthene	3640	210	8.1	310**	7.7
2,4-Dinitrophenol	1300	896**	6.1	23**	15.7
2,4-Dinitrotoluene	1900	1150	5.4	585	54.4
Hexachlorobenzene	1840	3.7	12.0	10	173.2
gamma BHC (Lindane)	7440	230	16.3	1240	55.2
beta BHC	640	35	13.3	65.3	51.7
METALS					
Lead	5000	70	4.3	10	51.7
Cadmium	1000	387	2.3	91	71.3

* - Triplicate analyses.
** - Duplicate analyses; one value was rejected as an outlier at the 90% confidence level using the Dixon Q test.

TABLE 7 - METHOD 1312 PRECISION RESULTS FOR VOLATILES

Compound Name	Soil No. 1 (Western) Avg. %Rec.*	%RSD	Soil No. 2 (Eastern) Avg. %Rec.*	%RSD	Soil No. 3 (Western and Sludge) Avg. %Rec.**	%RSD	Soil No. 4 (Western and Sludge) Avg. %Rec.***	%RSD
Acetone	44.0	12.4	43.8	2.25	116.0	11.5	21.3	71.4
Acrylonitrile	52.5	68.4	50.5	70.0	49.3	44.9	51.8	4.6
Benzene	47.8	8.29	34.8	16.3	49.8	36.7	33.4	41.1
n-Butyl Alcohol (1-Butanol)	55.5	2.91	49.2	14.6	65.5	37.2	73.0	13.9
Carbon disulfide	21.4	16.4	12.9	49.5	36.5	51.5	21.3	31.5
Carbon tetrachloride	40.6	18.6	22.3	29.1	36.2	41.4	24.0	34.0
Chlorobenzene	64.4	6.76	41.5	13.1	44.2	32.0	33.0	24.9
Chloroform	61.3	8.04	54.8	16.4	61.8	29.1	45.8	38.6
1,2-Dichloroethane	73.4	4.59	68.7	11.3	58.3	33.3	41.2	37.8
1,1-Dichloroethane	31.4	14.5	22.9	39.3	32.0	54.4	16.8	26.4
Ethyl acetate	76.4	9.65	75.4	4.02	23.0	119.8	11.0	115.5
Ethylbenzene	56.2	9.22	23.2	11.5	37.5	36.1	27.2	28.6
Ethyl ether	48.0	16.4	55.1	9.72	37.3	31.2	42.0	17.6
Isobutanol (4-Methyl -1-propanol)	0.0	ND	0.0	ND	61.8	37.7	76.0	12.2
Methylene chloride	47.5	30.3	42.2	42.9	52.0	37.4	37.3	16.6
Methyl ethyl ketone (2-Butanone)	56.7	5.94	61.9	3.94	73.7	31.3	40.6	39.0
Methyl isobutyl ketone	81.1	10.3	88.9	2.99	58.3	32.6	39.8	40.3
1,1,1,2-Tetrachloroethane	69.0	6.73	41.1	11.3	50.8	31.5	36.8	23.8
1,1,2,2-Tetrachloroethane	85.3	7.04	58.9	4.15	64.0	25.7	53.6	15.8
Tetrachloroethene	45.1	12.7	15.2	17.4	26.2	44.0	18.6	24.2
Toluene	59.2	8.06	49.3	10.5	45.7	35.2	31.4	37.2
1,1,1-Trichloroethane	47.2	16.0	33.8	22.8	40.7	40.6	26.2	38.8
1,1,2-Trichloroethane	76.2	5.72	67.3	8.43	61.7	28.0	46.4	25.4
Trichloroethene	54.5	11.1	39.4	19.5	38.8	40.9	25.6	34.1
Trichlorofluoromethane	20.7	24.5	12.6	60.1	28.5	34.0	19.8	33.9
1,1,2-Trichlorotrifluoroethane	18.1	26.7	6.95	58.0	21.5	67.8	15.3	24.8
Vinyl chloride	10.2	20.3	7.17	72.8	25.0	61.0	11.8	25.4

* Triplicate analyses
** Six replicate analyses
*** Five replicate analyses

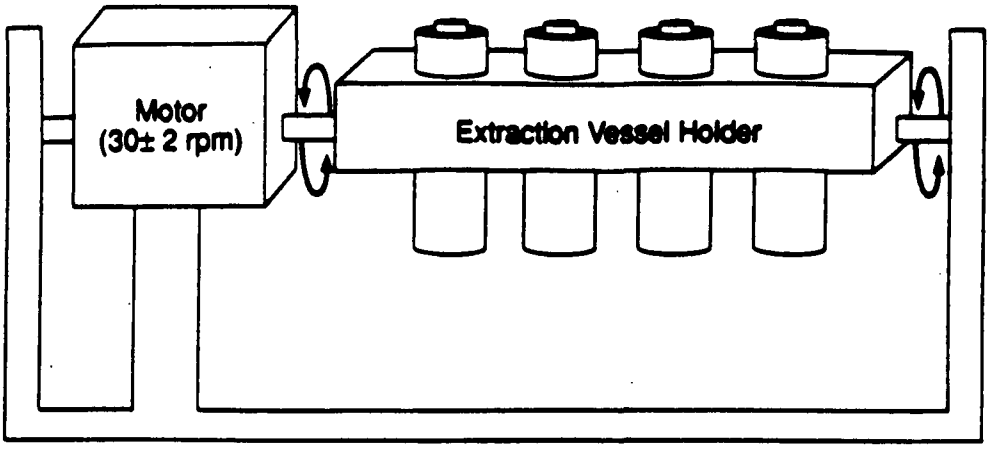


Figure 1. Rotary Agitation Apparatus

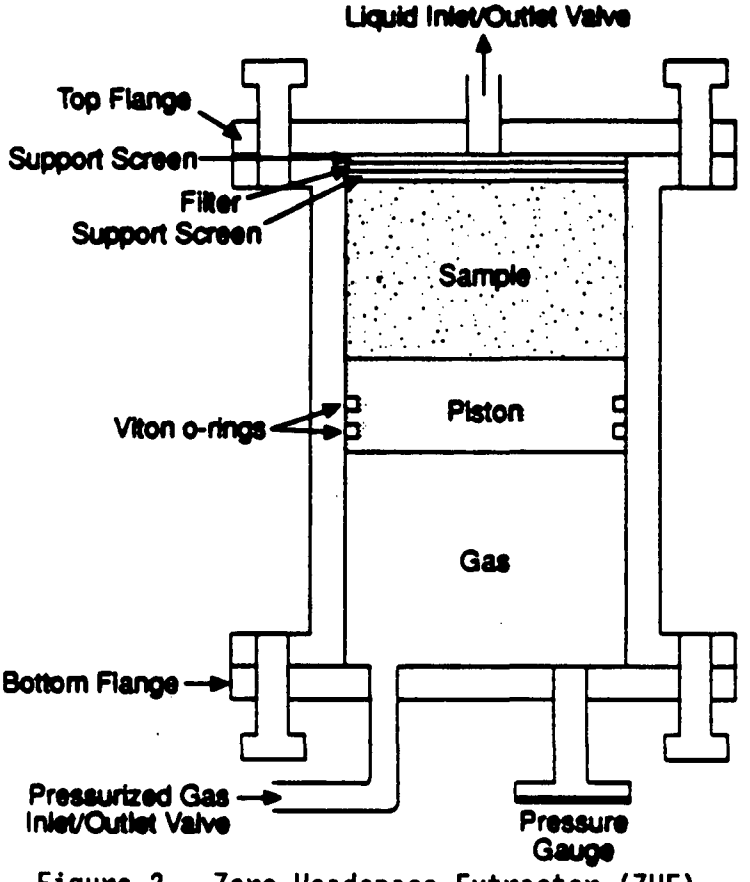
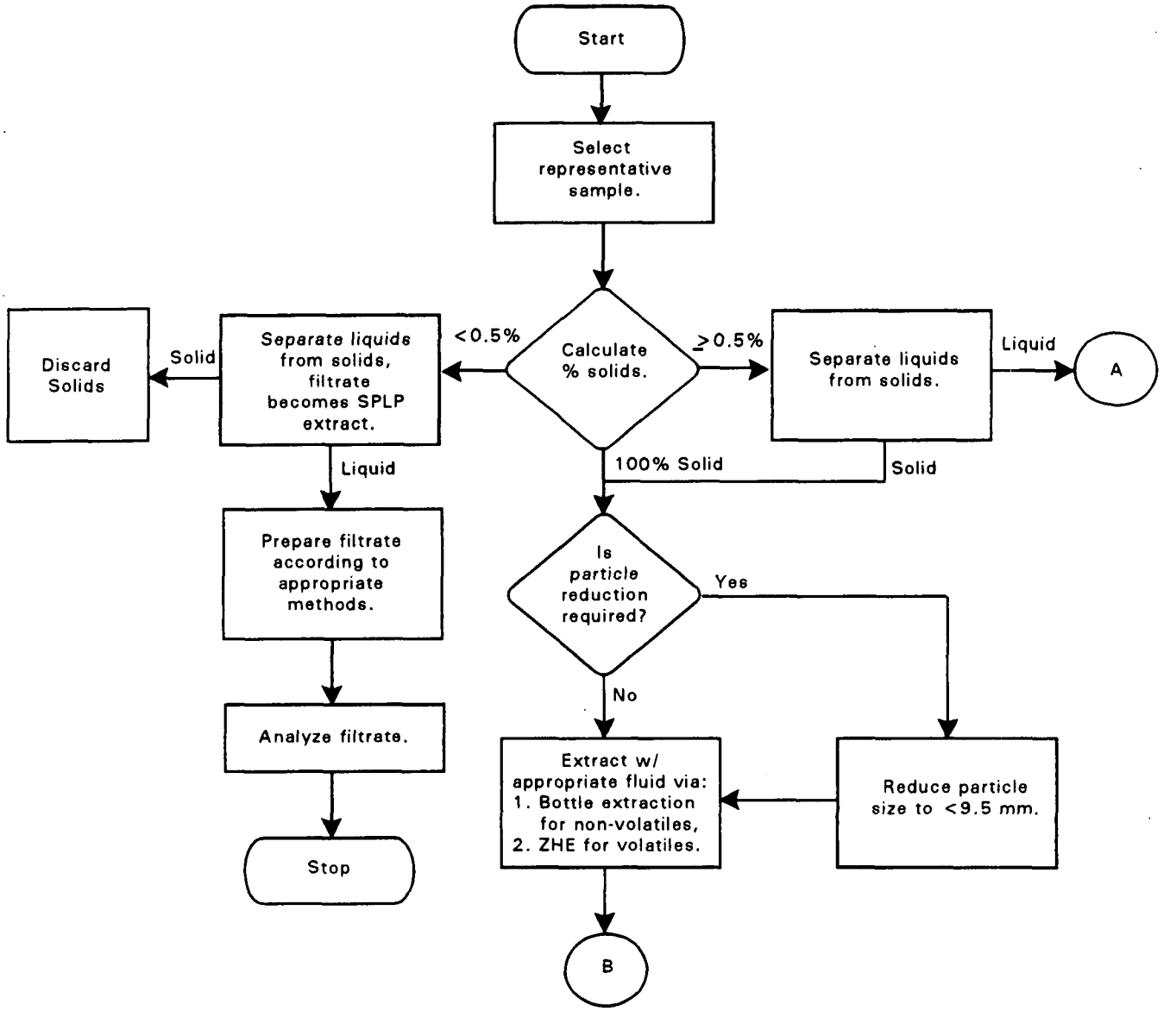


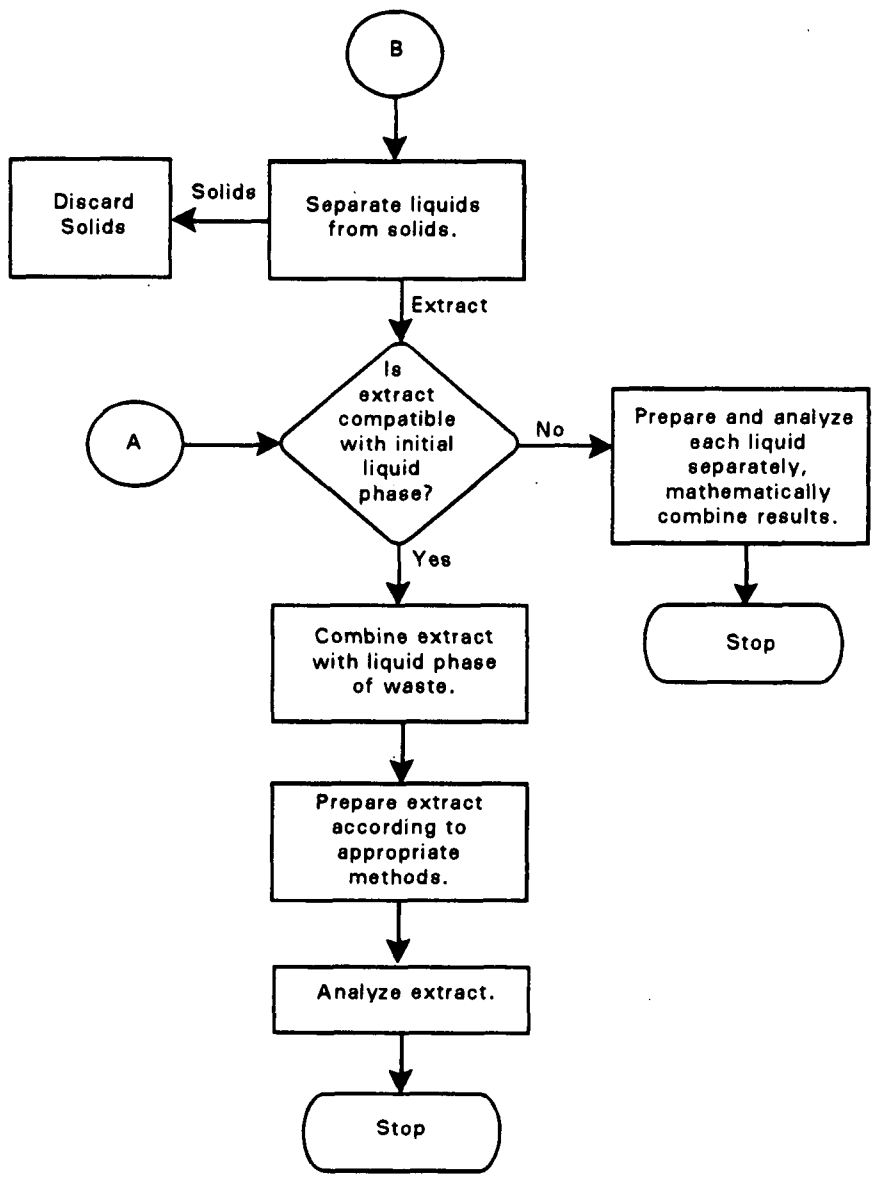
Figure 2. Zero-Headspace Extractor (ZHE)

METHOD 1312

SYNTHETIC PRECIPITATION LEACHING PROCEDURE



SYNTHETIC PRECIPITATION LEACHING PROCEDURE (continued)



METHOD 1320

MULTIPLE EXTRACTION PROCEDURE

1.0 SCOPE AND APPLICATION

The Multiple Extraction Procedure (MEP) described in this method is designed to simulate the leaching that a waste will undergo from repetitive precipitation of acid rain on an improperly designed sanitary landfill. The repetitive extractions reveal the highest concentration of each constituent that is likely to leach in a natural environment. Method 1320 is applicable to liquid, solid, and multiphase samples.

2.0 SUMMARY OF METHOD

Waste samples are extracted according to the Extraction Procedure Toxicity Test (Method 1310, Chapter 8) and analyzed for the constituents of concern listed in Chapter 7, Table 7-1: Maximum Concentration of Contaminants for Characteristic of EP Toxicity, using the 7000 and 8000 series methods. Then the solid portions of the samples that remain after application of Method 1310 are re-extracted nine times using synthetic acid rain extraction fluid. If the concentration of any constituent of concern increases from the 7th or 8th extraction to the 9th extraction, the procedure is repeated until these concentrations decrease.

3.0 INTERFERENCES

Potential interferences that may be encountered during analysis are discussed in the appropriate analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Refer to Method 1310.

5.0 REAGENTS

5.1 Refer to Method 1310.

5.2 Sulfuric acid:nitric acid, 60/40 weight percent mixture: Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to Method 1310.

7.0 PROCEDURE

7.1 Run the Extraction Procedure (EP) test in Method 1310.

7.2 Analyze the extract for the constituents of interest.

7.3 Prepare a synthetic acid rain extraction fluid by adding the 60/40 weight percent sulfuric acid and nitric acid to distilled deionized water until the pH is 3.0 $\pm$ 0.2.

7.4 Take the solid phase of the sample remaining after the Separation Procedure of the Extraction Procedure and weigh it. Measure an aliquot of synthetic acid rain extraction fluid equal to 20 times the weight of the solid sample. Do not allow the solid sample to dry before weighing.

7.5 Combine the solid phase sample and acid rain fluid in the same extractor as used in the EP and begin agitation. Record the pH within 5-10 min after agitation has been started.

7.6 Agitate the mixture for 24 hr, maintaining the temperature at 20-40°C (68-104°F). Record the pH at the end of the 24-hr extraction period.

7.7 Repeat the Separation Procedure as described in Method 1310.

7.8 Analyze the extract for the constituents of concern.

7.9 Repeat steps 7.4-7.8 eight additional times.

7.10 If, after completing the ninth synthetic rain extraction, the concentration of any of the constituents of concern is increasing over that found in the 7th and 8th extractions, then continue extracting with synthetic acid rain until the concentration in the extract ceases to increase.

7.11 Report the initial and final pH of each extraction and the concentration of each listed constituent of concern in each extract.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 All quality control measures suggested in the referenced analytical methods should be followed.

9.0 METHOD PERFORMANCE

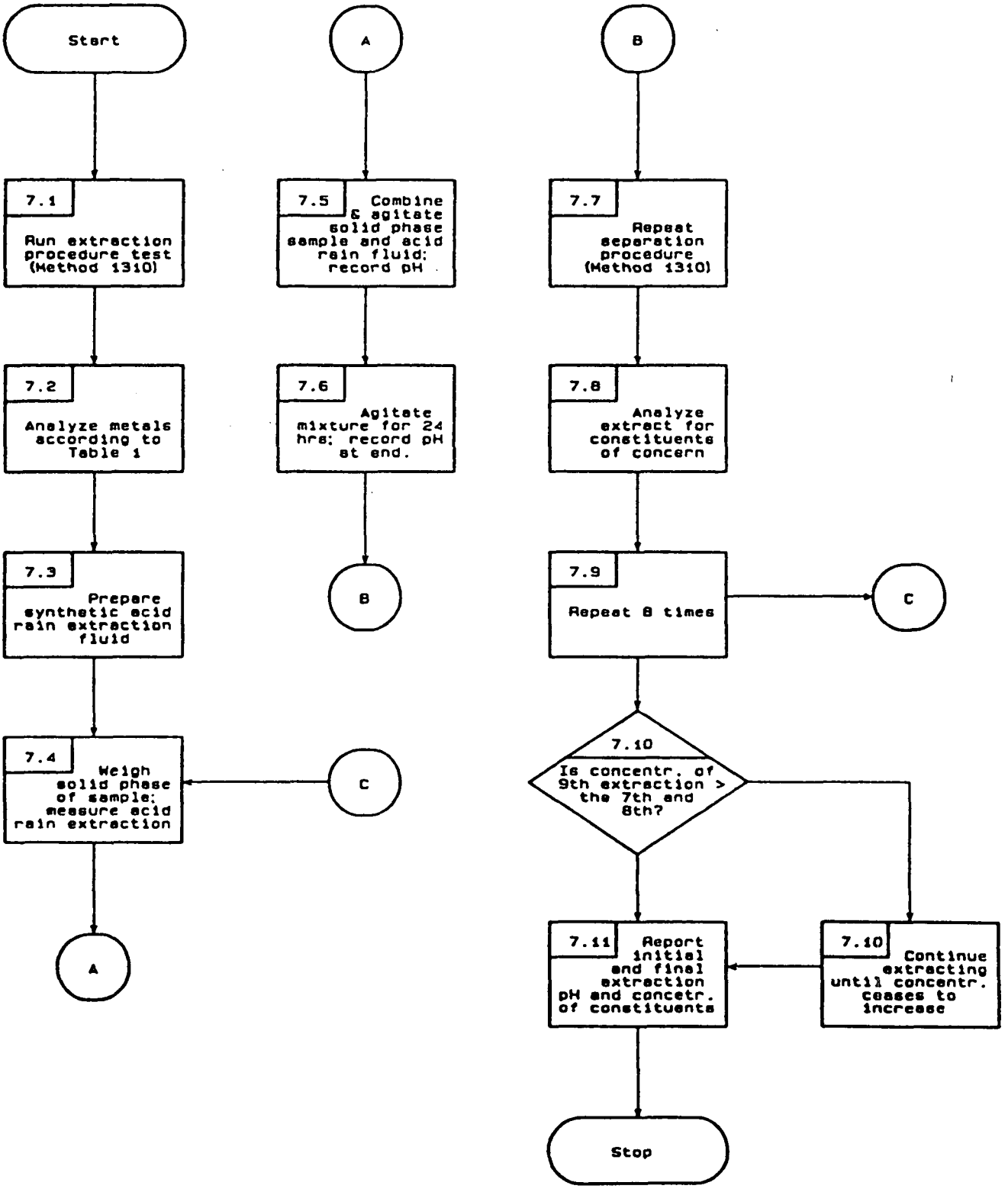
9.1 No data provided.

10.0 REFERENCES

10.1 None required.

METHOD 1320

MULTIPLE EXTRACTION PROCEDURE



METHOD 1330A

EXTRACTION PROCEDURE FOR OILY WASTES

1.0 SCOPE AND APPLICATION

1.1 Method 1330 is used to determine the mobile metal concentration (MMC) in oily wastes.

1.2 Method 1330 is applicable to API separator sludges, rag oils, slop oil emulsions, and other oil wastes derived from petroleum refining.

2.0 SUMMARY OF METHOD

2.1 The sample is separated into solid and liquid components by filtration.

2.2 The solid phase is placed in a Soxhlet extractor, charged with tetrahydrofuran, and extracted. The THF is removed, the extractor is then charged with toluene, and the sample is reextracted.

2.3 The EP method (Method 1310) is run on the dry solid residue.

2.4 The original liquid, combined extracts, and EP leachate are analyzed for the EP metals.

3.0 INTERFERENCES

3.1 Matrix interferences will be coextracted from the sample. The extent of these interferences will vary considerably from waste to waste, depending on the nature and diversity of the particular refinery waste being analyzed.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extraction apparatus.

4.2 Vacuum pump or other source of vacuum.

4.3 Buchner funnel 12.

4.4 Electric heating mantle.

4.5 Paper extraction thimble.

4.6 Filter paper.

4.7 Muslin cloth disks.

4.8 Evaporative flask - 250-mL.

4.9 Balance - Analytical, capable of weighing to $\pm$ 0.5 mg.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Tetrahydrofuran, C_4H_8O.

5.4 Toluene, $C_6H_5CH_3$.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Samples must be collected in glass containers having a total volume of at least 150 mL. No solid material should interfere with sealing the sample container.

6.2 Sampling devices should be wiped clean with paper towels or absorbent cloth, rinsed with a small amount of hexane followed by acetone rinse, and dried between samples. Alternatively, samples can be taken with disposable sampling devices in beakers.

7.0 PROCEDURE

7.1 Separate the sample (minimum 100 g) into its solid and liquid components. The liquid component is defined as that portion of the sample which passes through a 0.45 μm filter media under a pressure differential of 75 psi.

7.2 Determine the quantity of liquid (mL) and the concentration of the toxicants of concern in the liquid phase (mg/L).

7.3 Place the solid phase into a Soxhlet extractor, charge the concentration flask with 300 mL tetrahydrofuran, and extract for 3 hours.

7.4 Remove the flask containing tetrahydrofuran and replace it with one containing 300 mL toluene.

7.5 Extract the solid a second time, for 3 hours, with the toluene.

7.6 Combine the tetrahydrofuran and toluene extracts.

7.7 Analyze the combined extracts for the toxicants of concern.

7.8 Determine the quantity of liquid (mL) and the concentration of the toxicants of concern in the combined extracts (mg/L).

7.9 Take the solid material remaining in the Soxhlet thimble and dry it at 100°C for 30 minutes.

7.10 Run the EP (Method 1310) on the dried solid.

7.11 Calculate the mobile metal concentration (MMC) in mg/L using the following formula:

$$MMC = 1{,}000 \times \frac{(Q_1 + Q_2 + Q_3)}{(L_1 + L_2 + L_3)}$$

where:

Q_1 = Mass of toxicant in initial liquid phase of sample (amount of liquid x concentration of toxicant) (mg).

Q_2 = Mass of toxicant in combined organic extracts of sample (amount of liquid x concentration of toxicant) (mg).

Q_3 = Mass of toxicant in EP extract of solid (amount of extract x concentration of toxicant) (mg).

L_1 = Volume of initial liquid (mL).

L_2 = Volume of liquid in THF and toluene extract (Step 7.8) (mL).

L_3 = Volume of liquid in EP (mL) = 20 x [weight of dried solid from Step 7.9 (g)].

8.0 QUALITY CONTROL

8.1 Any reagent blanks or replicates samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

Figure 1. Extractor

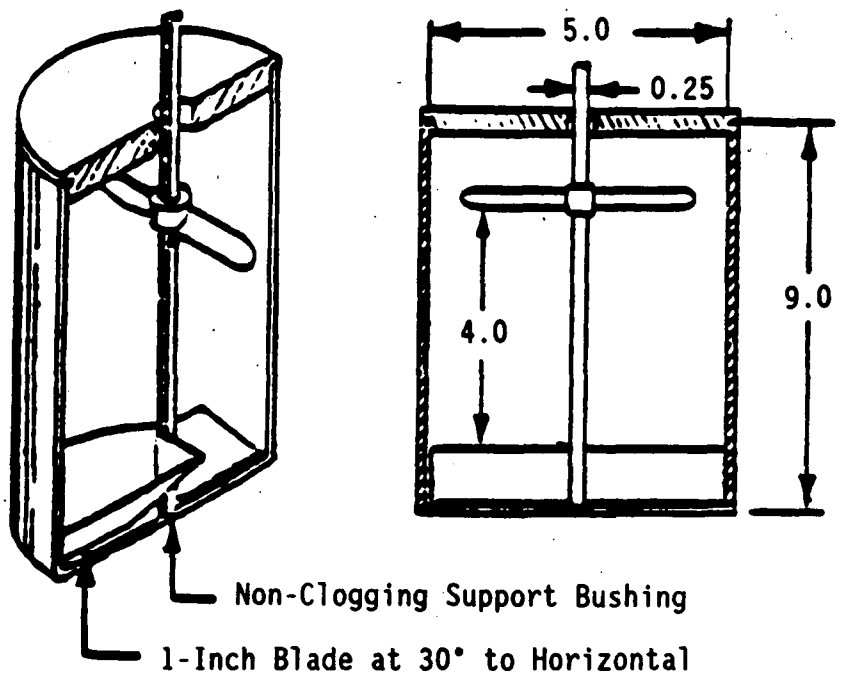


Figure 2. Rotary Extractor

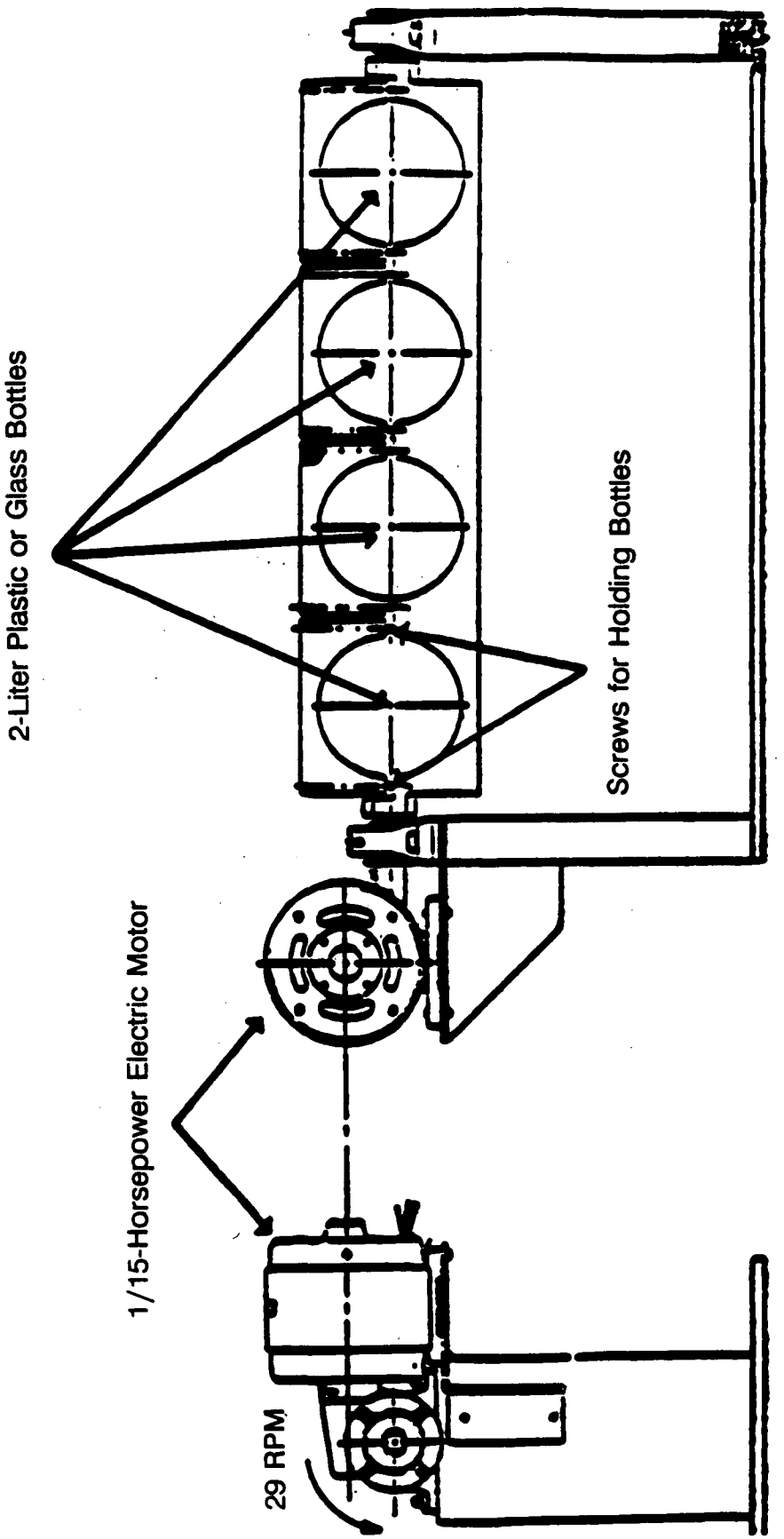


Figure 3. EPRI Extractor

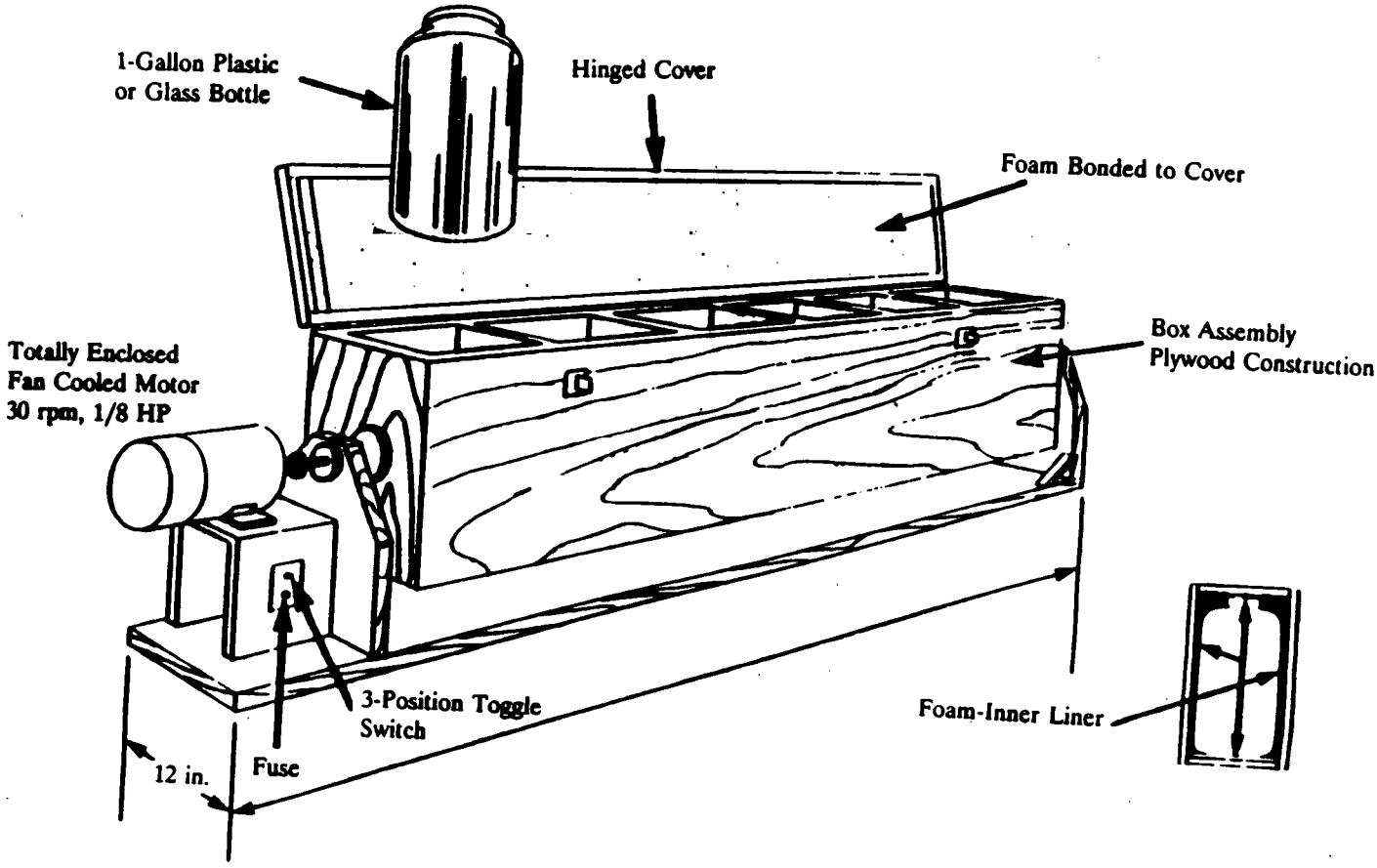
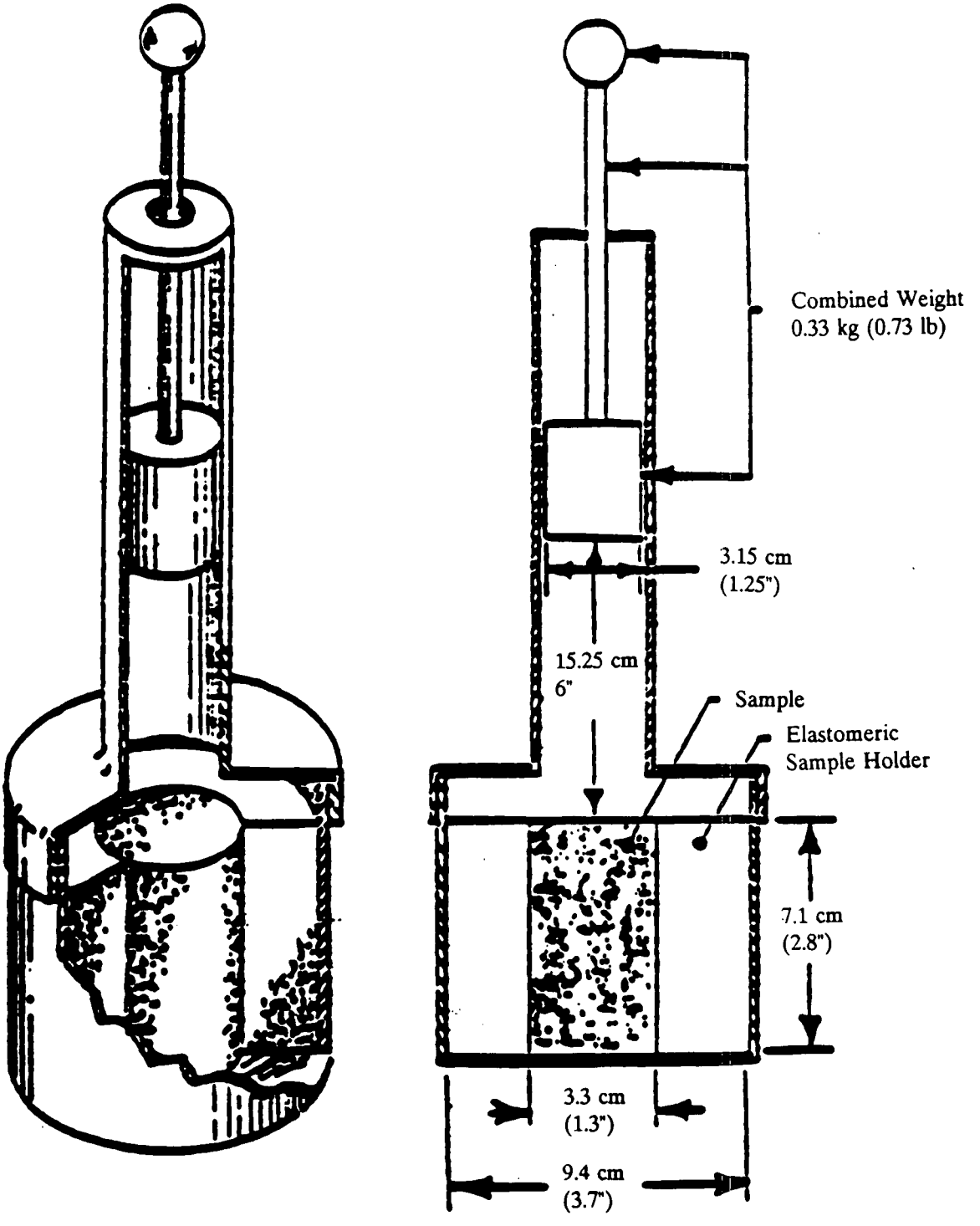
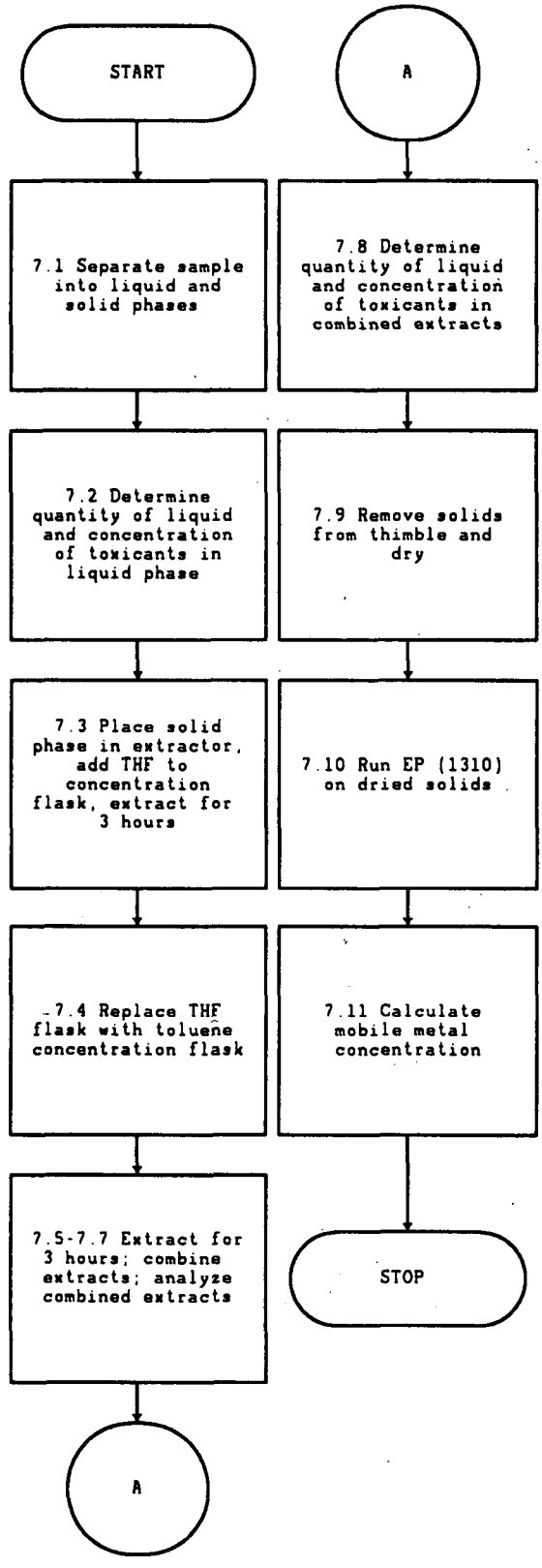


Figure 4. Compaction Tester



METHOD 1330A
EXTRACTION PROCEDURE FOR OILY WASTE



METHOD 9040A

pH ELECTROMETRIC MEASUREMENT

1.0 SCOPE AND APPLICATION

1.1 Method 9040 is used to measure the pH of aqueous wastes and those multiphase wastes where the aqueous phase constitutes at least 20% of the total volume of the waste.

1.2 The corrosivity of concentrated acids and bases, or of concentrated acids and bases mixed with inert substances, cannot be measured. The pH measurement requires some water content.

2.0 SUMMARY

2.1 The pH of the sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode. The measuring device is calibrated using a series of standard solutions of known pH.

3.0 INTERFERENCES

3.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants, or moderate (<0.1 molar solution) salinity.

3.2 Sodium error at pH levels >10 can be reduced or eliminated by using a low-sodium-error electrode.

3.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by rinsing with distilled water. An additional treatment with hydrochloric acid (1:10) may be necessary to remove any remaining film.

3.4 Temperature effects on the electrometric determination of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference should be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source of temperature effects is the change of pH due to changes in the sample as the temperature changes. This error is sample-dependent and cannot be controlled. It should, therefore, be noted by reporting both the pH and temperature at the time of analysis.

4.0 APPARATUS AND MATERIALS

4.1 pH meter: Laboratory or field model. Many instruments are commercially available with various specifications and optional equipment.

4.2 Glass electrode.

4.3 Reference electrode: A silver-silver chloride or other reference electrode of constant potential may be used.

NOTE: Combination electrodes incorporating both measuring and referenced functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

4.4 Magnetic stirrer and Teflon-coated stirring bar.

4.5 Thermometer and/or temperature sensor for automatic compensation.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Primary standard buffer salts are available from the National Institute of Standards and Technology (NIST) and should be used in situations where extreme accuracy is necessary. Preparation of reference solutions from these salts requires some special precautions and handling, such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

5.3 Secondary standard buffers may be prepared from NIST salts or purchased as solutions from commercial vendors. These commercially available solutions have been validated by comparison with NIST standards and are recommended for routine use.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples should be analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration:

7.1.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.1.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart. (For corrosivity characterization, the calibration of the pH meter should include a buffer of pH 2 for acidic wastes and a pH 12 buffer for caustic wastes.) Various

instrument designs may involve use of a dial (to "balance" or "standardize") or a slope adjustment, as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value.

7.2 Place the sample or buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar. If field measurements are being made, the electrodes may be immersed directly into the sample stream to an adequate depth and moved in a manner to ensure sufficient sample movement across the electrode-sensing element as indicated by drift-free readings (<0.1 pH).

7.3 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected. Instruments are equipped with automatic or manual compensators that electronically adjust for temperature differences. Refer to manufacturer's instructions.

7.4 Thoroughly rinse and gently wipe the electrodes prior to measuring pH of samples. Immerse the electrodes into the sample beaker or sample stream and gently stir at a constant rate to provide homogeneity and suspension of solids. Note and record sample pH and temperature. Repeat measurement on successive aliquots of sample until values differ by <0.1 pH units. Two or three volume changes are usually sufficient.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for the appropriate QC protocols.

8.2 Electrodes must be thoroughly rinsed between samples.

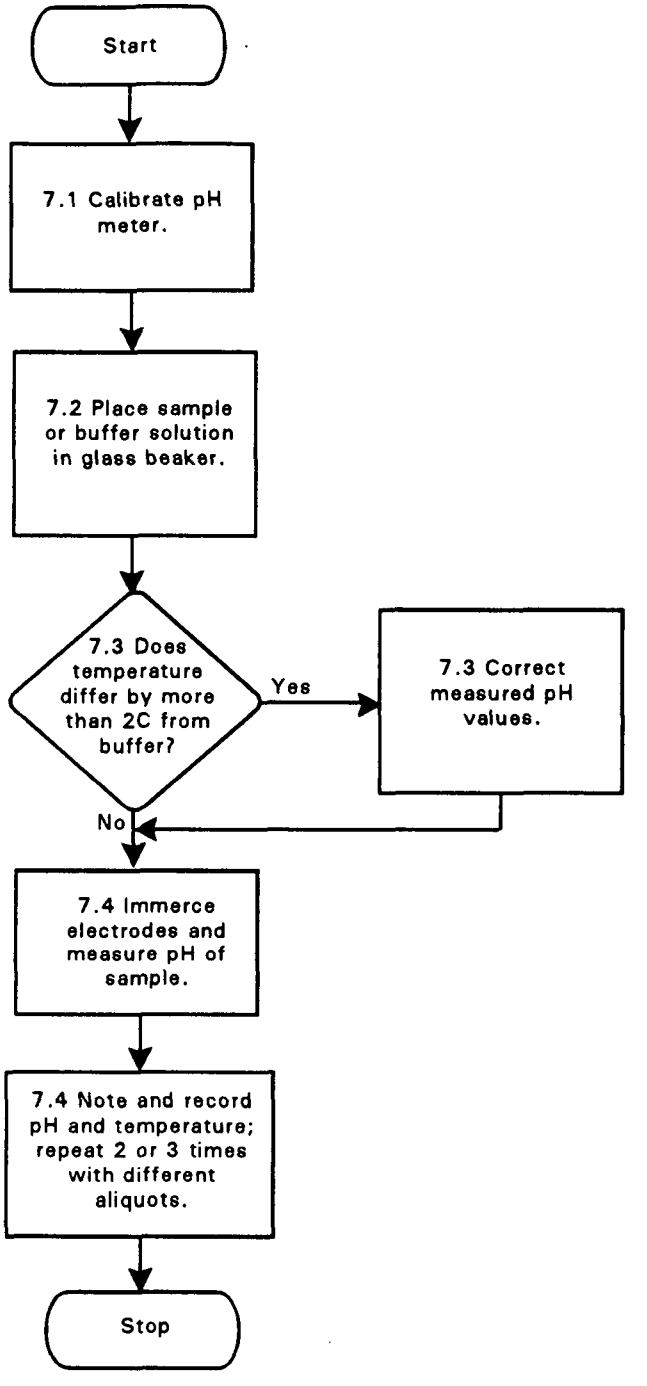
9.0 METHOD PERFORMANCE

9.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

		Accuracy as	
pH Units	Standard Deviation pH Units	Bias %	Bias pH Units
3.5	0.10	-0.29	-0.01
3.5	0.11	-0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	-0.03	-0.002
8.0	0.13	-0.12	-0.01
8.0	0.12	+0.16	+0.01

10.0 REFERENCES

1. National Bureau of Standards, Standard Reference Material Catalog 1986-87, Special Publication 260.


Start
7.1 Calibrate pH meter.
7.2 Place sample or buffer solution in glass beaker.
7.3 Does temperature differ by more than 2C from buffer?
Yes
7.3 Correct measured pH values.
No
7.4 Immerce electrodes and measure pH of sample.
7.4 Note and record pH and temperature; repeat 2 or 3 times with different aliquots.
Stop

METHOD 9041A

pH PAPER METHOD

1.0 SCOPE AND APPLICATION

1.1 Method 9041 may be used to measure pH as an alternative to Method 9040 (except as noted in Step 1.3) or in cases where pH measurements by Method 9040 are not possible.

1.2 Method 9041 is not applicable to wastes that contain components that may mask or alter the pH paper color change.

1.3 pH paper is not considered to be as accurate a form of pH measurement as pH meters. For this reason, pH measurements taken with Method 9041 cannot be used to define a waste as corrosive or noncorrosive (see RCRA regulations 40 CFR §261.22(a)(1).

2.0 SUMMARY OF METHOD

2.1 The approximate pH of the waste is determined with wide-range pH paper. Then a more accurate pH determination is made using "narrow-range" pH paper whose accuracy has been determined (1) using a series of buffers or (2) by comparison with a calibrated pH meter.

3.0 INTERFERENCES

3.1 Certain wastes may inhibit or mask changes in the pH paper. This interference can be determined by adding small amounts of acid or base to a small aliquot of the waste and observing whether the pH paper undergoes the appropriate changes.

CAUTION: THE ADDITION OF ACID OR BASE TO WASTES MAY RESULT IN VIOLENT REACTIONS OR THE GENERATION OF TOXIC FUMES (e.g., hydrogen cyanide). Thus, a decision to take this step requires some knowledge of the waste. See Step 7.3.3 for additional precautions.

4.0 APPARATUS AND MATERIALS

4.1 Wide-range pH paper.

4.2 Narrow-range pH paper: With a distinct color change for every 0.5 pH unit (e.g., Alkaacid Full-Range pH Kit, Fisher Scientific or equivalent). Each batch of narrow-range pH paper must be calibrated versus certified pH buffers or by comparison with a pH meter which has been calibrated with certified pH buffers. If the incremental reading of the narrow-range pH paper is within 0.5 pH units, then the agreement between the buffer or the calibrated pH meter with the paper must be within 0.5 pH units.

4.3 pH Meter (optional).

5.0 REAGENTS

5.1 Certified pH buffers: To be used for calibrating the pH paper or for calibrating the pH meter that will be used subsequently to calibrate the pH paper.

5.2 Dilute acid (e.g., 1:4 HCl).

5.3 Dilute base (e.g., 0.1 N NaOH).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan which addresses the considerations discussed in Chapter Nine of this manual.

7.0 PROCEDURE

7.1 A representative aliquot of the waste must be tested with wide-range pH paper to determine the approximate pH.

7.2 The appropriate narrow-range pH paper is chosen and the pH of a second aliquot of the waste is determined. This measurement should be performed in duplicate.

7.3 Identification of interference:

7.3.1 Take a third aliquot of the waste, approximately 2 mL in volume, and add acid dropwise until a pH change is observed. Note the color change.

7.3.2 Add base dropwise to a fourth aliquot and note the color change. (Wastes that have a buffering capacity may require additional acid or base to result in a measurable pH change.)

7.3.3 The observation of the appropriate color change is a strong indication that no interferences have occurred.

CAUTION ADDITION OF ACID OR BASE TO SAMPLES MAY RESULT IN VIOLENT REACTIONS OR THE GENERATION OF TOXIC FUMES. PRECAUTIONS MUST BE TAKEN. THE ANALYST SHOULD PERFORM THESE TESTS IN A WELL-VENTILATED HOOD WHEN DEALING WITH UNKNOWN SAMPLES.

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for easy reference or inspection.

8.2 All pH determinations must be performed in duplicate.

8.3 Each batch of pH paper must be calibrated versus certified pH buffers or a pH meter which has been calibrated with certified pH buffers.

9.0 METHOD PERFORMANCE

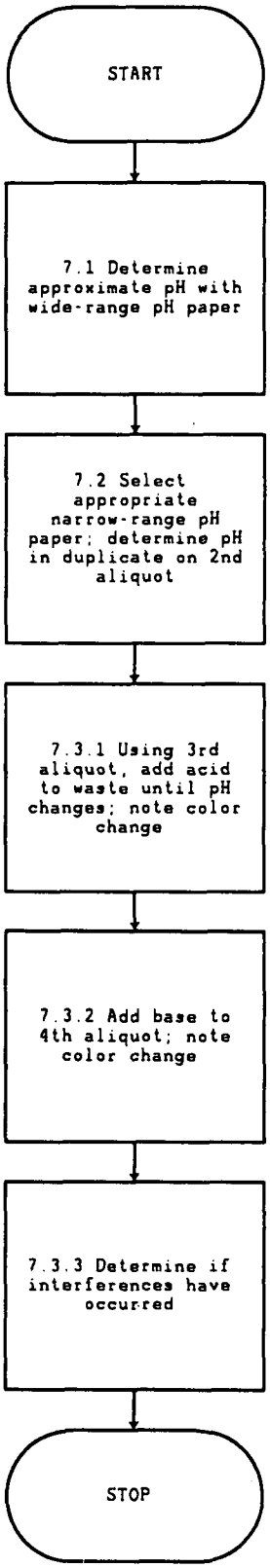
9.1 No data provided.

10.0 REFERENCES

10.1 None required.

METHOD 9041A

pH PAPER METHOD



METHOD 9045B

SOIL AND WASTE pH

1.0 SCOPE AND APPLICATION

1.1 Method 9045 is an electrometric procedure for measuring pH in soils and waste samples. Wastes may be solids, sludges, or non-aqueous liquids. If water is present, it must constitute less than 20% of the total volume of the sample.

2.0 SUMMARY OF METHOD

2.1 The sample is mixed with reagent water, and the pH of the resulting aqueous solution is measured.

3.0 INTERFERENCES

3.1 Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strong acid solutions, with a true pH of <1, may give incorrectly high pH measurements.

3.2 Temperature fluctuations will cause measurement errors.

3.3 Errors will occur when the electrodes become coated. If an electrode becomes coated with an oily material that will not rinse free, the electrode can (1) be cleaned with an ultrasonic bath, or (2) be washed with detergent, rinsed several times with water, placed in 1:10 HCl so that the lower third of the electrode is submerged, and then thoroughly rinsed with water, or (3) be cleaned per the manufacturer's instructions.

4.0 APPARATUS AND MATERIALS

4.1 pH Meter with means for temperature compensation.

4.2 Glass Electrode.

4.3 Reference electrode: A silver-silver chloride or other reference electrode of constant potential may be used.

> NOTE: Combination electrodes incorporating both measuring and referenced functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

4.4 Beaker: 50-mL.

4.5 Thermometer and/or temperature sensor for automatic compensation.

4.6 Analytical balance: capable of weighing 0.1 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Primary standard buffer salts are available from the National Institute of Standards and Technology (NIST) and should be used in situations where extreme accuracy is necessary. Preparation of reference solutions from these salts requires some special precautions and handling, such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

5.4 Secondary standard buffers may be prepared from NIST salts or purchased as solutions from commercial vendors. These commercially available solutions, which have been validated by comparison with NIST standards, are recommended for routine use.

6.0 SAMPLE PRESERVATION AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples should be analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration:

7.1.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.1.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart. Repeat adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value.

7.2 Sample preparation and pH measurement of soils:

7.2.1 To 20 g of soil in a 50-mL beaker, add 20 mL of reagent water, cover, and continuously stir the suspension for 5 minutes. .

Additional dilutions are allowed if working with hygroscopic soils and salts or other problematic matrices.

7.2.2 Let the soil suspension stand for about 1 hour to allow most of the suspended clay to settle out from the suspension or filter or centrifuge off the aqueous phase for pH measurement.

7.2.3 Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant solution to establish a good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrodes into the sample solution in this manner. For combination electrodes, immerse just below the suspension.

7.2.4 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected.

7.2.5 Report the results as "soil pH measured in water at __ °C" where "__°C" is the temperature at which the test was conducted.

7.3 Sample preparation and pH measurement of waste materials:

7.3.1 To 20 g of waste sample in a 50-mL beaker, add 20 mL of reagent water, cover, and continuously stir the suspension for 5 minutes. . Additional dilutions are allowed if working with hygroscopic wastes and salts or other problematic matrices.

7.3.2 Let the waste suspension stand for about 15 minutes to allow most of the suspended waste to settle out from the suspension or filter or centrifuge off aqueous phase for pH measurement.

NOTE: If the waste is hygroscopic and absorbs all the reagent water, begin the experiment again using 20 g of waste and 40 mL of reagent water.

NOTE: If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase. The electrode may need to be cleaned (Step 3.3) if it becomes coated with an oily material.

7.3.3 Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant to establish good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrode into the sample solution in this manner. For combination electrodes, immerse just below the suspension.

7.3.4 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected.

7.3.5 Report the results as "waste pH measured in water at __ °C" where "__°C" is the temperature at which the test was conducted.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for the appropriate QC protocols.

8.2 Electrodes must be thoroughly rinsed between samples.

9.0 METHOD PERFORMANCE

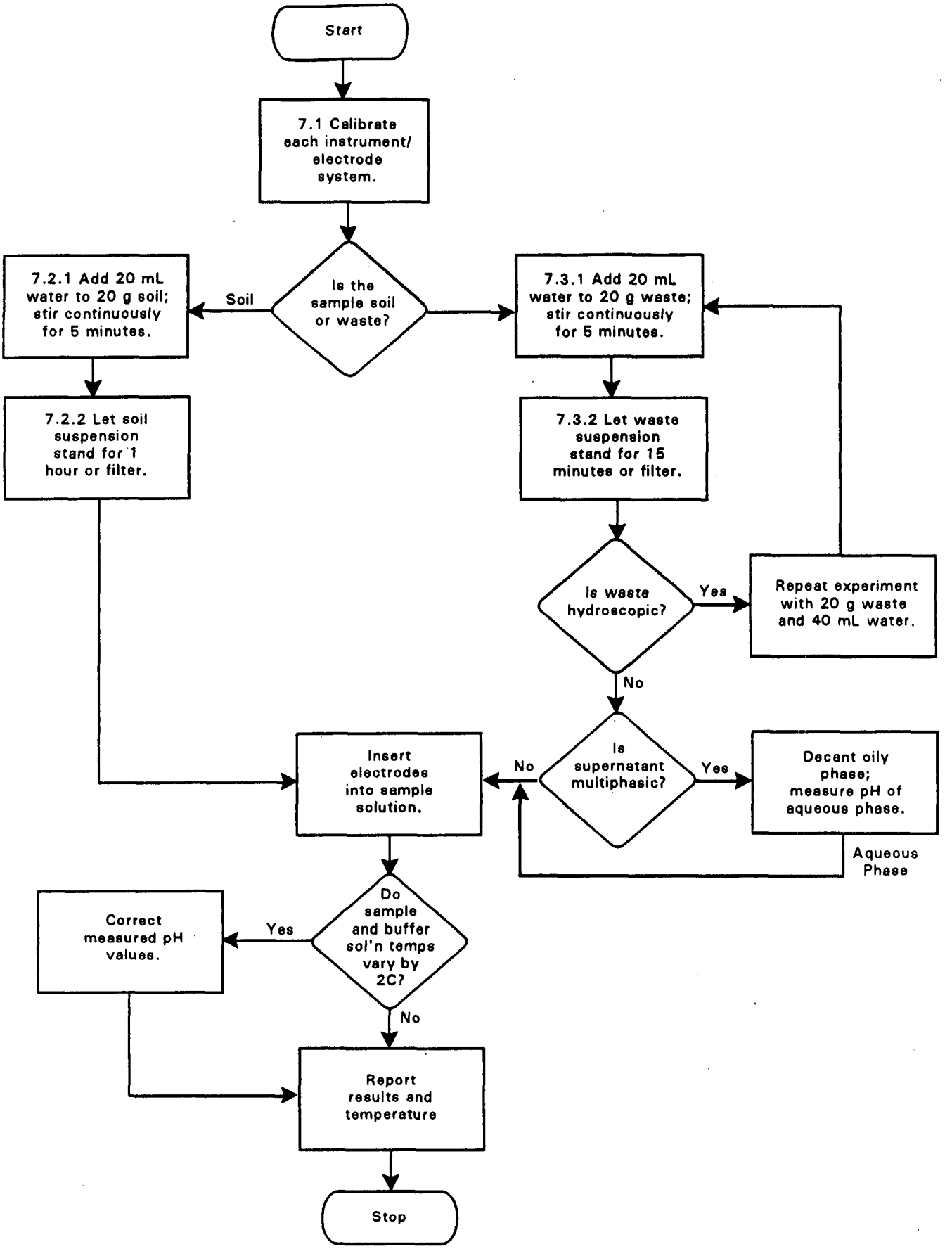
9.1 No data provided.

10.0 REFERENCES

1. Black, Charles Allen; Methods of Soil Analysis; American Society of Agronomy: Madison, WI, 1973.

2. National Bureau of Standards, Standard Reference Material Catalog, 1986-87, Special Publication 260.

SOIL AND WASTE pH



METHOD 9050

SPECIFIC CONDUCTANCE

1.0 SCOPE AND APPLICATION

1.1 Method 9050 is used to measure the specific conductance of drinking, ground, surface, and saline waters and domestic and industrial aqueous wastes. Method 9050 is not applicable to solid samples.

2.0 SUMMARY OF METHOD

2.1 The specific conductance of a sample is measured using a self-contained conductivity meter (Wheatstone bridge-type or equivalent).

2.2 Whenever possible, samples are analyzed at 25°C. If samples are analyzed at different temperatures, temperature corrections must be made and results reported at 25°C.

3.0 INTERFERENCES

3.1 Platinum electrodes can degrade and cause erratic results. When this happens, as evidenced by erratic results or flaking off of the platinum black, the electrode should be replatinized.

3.2 The specific conductance cell can become coated with oil and other materials. It is essential that the cell be thoroughly rinsed and, if necessary, cleaned between samples.

4.0 APPARATUS AND MATERIALS

4.1 Self-contained conductivity instruments: an instrument consisting of a source of alternating current, a Wheatstone bridge, null indicator, and a conductivity cell or other instrument measuring the ratio of alternating current through the cell to voltage across it. The latter has the advantage of a linear reading of conductivity. Choose an instrument capable of measuring conductivity with an error not exceeding 1% or 1 umho/cm, whichever is greater.

4.2 Platinum-electrode or non-platinum-electrode specific conductance cell.

4.3 Water bath.

4.4 Thermometer: capable of being read to the nearest 0.1°C and covering the range 23° to 27°C. An electrical thermometer having a small thermistor sensing element is convenient because of its rapid response.

5.0 REAGENTS

5.1 Conductivity water: Pass distilled water through a mixed-bed deionizer and discard first 1,000 mL. Conductivity should be less than 1 umho/cm.

5.2 Standard potassium chloride (0.0100 M): Dissolve 0.7456 g anhydrous KCl in conductivity water and make up to 1,000 mL at 25°C. This solution will have a specific conductance of 1,413 umho/cm at 25°C.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed and thoroughly rinsed. Both plastic and glass containers are suitable.

6.3 Aqueous samples should be stored at 4°C and analyzed within 24 hr.

7.0 PROCEDURE

7.1 Determination of cell constant: Rinse conductivity cell with at least three portions of 0.01 N KCl solution. Adjust temperature of a fourth portion to 25.0 ± 0.1°C. Measure resistance of this portion and note temperature. Compute cell constant, C:

$$C = (0.001413)(R_{KCl})\ 1 + 0.0191\ (t - 25)$$

where:

R_{KCl} = measured resistance, ohms; and

t = observed temperature, °C.

7.2 Conductivity measurement: Rinse cell with one or more portions of sample. Adjust temperature of a final portion to 25.0 ± 0.1°C. Measure sample resistance or conductivity and note temperature.

7.3 Calculation: The temperature coefficient of most waters is only approximately the same as that of standard KCl solution; the more the temperature of measurement deviates from 25.0°C, the greater the uncertainty in applying the temperature correction. Report all conductivities at 25.0°C.

7.3.1 When sample resistance is measured, conductivity at 25°C is:

$$K = \frac{(1{,}000{,}000)(C)}{R_m \; 1 + 0.0191 \; (t - 25)}$$

where:

K = conductivity, umho/cm;
C = cell constant, cm-L;
R_m = measured resistance of sample, ohms; and
t = temperature of measurement.

7.3.2 When sample conductivity is measured, conductivity at 25°C is:

$$K = \frac{(K_m)(1{,}000{,}000)(C)}{1 + 0.0191 \; (t - 25)}$$

where:

K_m = measured conductivity, umho at t°C, and other units are defined as above.

NOTE: If conductivity readout is in umho/cm, delete the factor 1,000,000 in the numerator.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Analyze check standards after approximately every 15 samples.

8.3 Run 1 duplicate sample for every 10 samples.

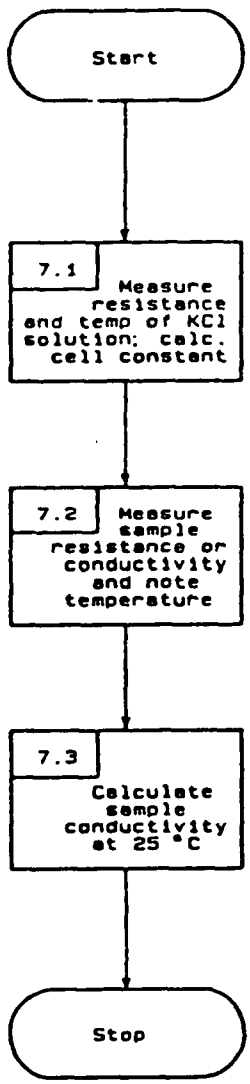
9.0 METHOD PERFORMANCE

9.1 Three synthetic samples were tested with the following results:

Conductivity umhos/cm	No. of Results	Relative Standard Deviation %	Relative Error %
147.0	117	8.6	9.4
303.0	120	7.8	1.9
228.0	120	8.4	3.0

10.0 REFERENCES

1. Standard Methods for the Examination of Water and Wastewater, 16th ed. (1985), Method 205.


Start
7.1
Measure resistance and temp of KCl solution; calc. cell constant
7.2
Measure sample resistance or conductivity and note temperature
7.3
Calculate sample conductivity at 25 °C
Stop

METHOD 9080

CATION-EXCHANGE CAPACITY OF SOILS (AMMONIUM ACETATE)

1.0 SCOPE AND APPLICATION

1.1 Method 9080 is used to determine the cation-exchange capacity of soils. The method is not applicable to soils containing appreciable amounts of vermiculite clays, kaolin, halloysite, or other 1:1-type clay minerals. They should be analyzed by the sodium acetate method (Method 9081). That method (9081) is also generally the preferred method for very calcareous soils. For distinctly acid soils, the cation-exchange capacity by summation method (Chapman, p. 900; see Paragraph 10.1) should be employed.

2.0 SUMMARY

2.1 The soil is mixed with an excess of 1 N ammonium acetate solution. This results in an exchange of the ammonium cations for exchangeable cations present in the soil. The excess ammonium is removed, and the amount of exchangeable ammonium is determined.

3.0 INTERFERENCES

3.1 Soils containing appreciable vermiculite clays, kaolin, halloysite, or other 1:1-type clay minerals will often give lower values for exchange capacity. See Paragraph 1.1 above.

3.2 With calcareous soils, the release of calcium carbonate from the soil into the ammonium acetate solution limits the saturation of exchange sites by the ammonium ion. This results in artificially low cation-exchange capacities.

4.0 APPARATUS AND MATERIALS

4.1 Erlenmeyer flask: 500-mL.

4.2 Buchner funnel or equivalent: 55-mm.

4.3 Sieve: 2-mm.

4.4 Aeration apparatus (assembled as in Figure 1):

4.4.1 **Kjeldahl flask:** 800-mL.

4.4.2 **Erlenmeyer flask:** 800-mL.

4.4.3 **Glass wool filter.**

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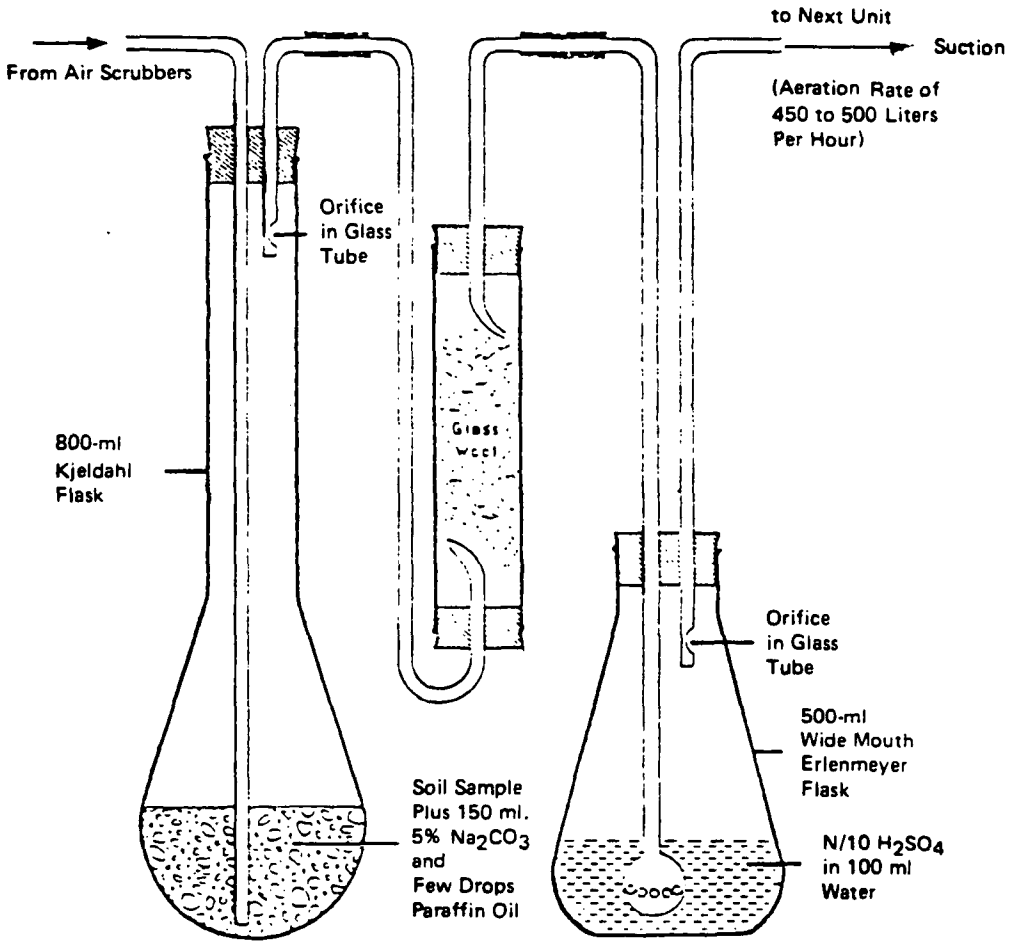


Figure 1. Diagram of aeration unit for determination of absorbed ammonia. Six to twelve such units is a convenient number for routine work; they can be mounted on a portable rack. (Apparatus as modified by Dr. A. P. Vanselow, Dept. of Soils & Plant Nutrition, Univerity of California, Riverside, Calif.).

4.4.4 **Glass tubing.**

4.4.5 **Flow meter.**

5.0 REAGENTS

5.1 Ammonium acetate (NH_4OAc), 1 N: Dilute 114 mL of glacial acetic acid (99.5%) with water to a volume of approximately 1 liter. Then add 138 mL of concentrated ammonium hydroxide (NH_4OH) and add water to obtain a volume of about 1,980 mL. Check the pH of the resulting solution, add more NH_4OH, as needed, to obtain a pH of 7, and dilute the solution to a volume of 2 liters with water.

5.2 Isopropyl alcohol: 99%.

5.3 Ammonium chloride (NH_4Cl), 1 N: Dissolve 53.49 g of NH_4Cl in Type II water, adjust the pH to 7.0 with NH_4OH, and dilute to 1 L.

5.4 Ammonium chloride (NH_4Cl), 0.25 N: Dissolve 13.37 g of NH_4Cl in Type II water, adjust the pH to 7.0 with NH_4OH, and dilute to 1 L.

5.5 Ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$), 10%: Add 90 mL of Type II water to 10 g of ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$) and mix well.

5.6 Dilute ammonium hydroxide (NH_4OH): Add 1 volume of concentrated NH_4OH to an equal volume of water.

5.7 Silver nitrate ($AgNO_3$), 0.10 N: Dissolve 15.39 g of $NgNO_3$ in Type II water, mix well, and dilute to 1 L.

5.8 Reagents for aeration option:

5.8.1 **Sodium carbonate solution** (Na_2CO_3), 5%: Add 95 mL of Type II water to 5 g of Na_2CO_3 and mix well.

5.8.2 **Paraffin oil.**

5.8.3 **Sulfuric acid** (H_2SO_4), 0.1 N standard: Add 2.8 mL concentrated H_2SO_4 to Type II water and dilute to 1 L. Standardize against a base of known concentration.

5.8.4 **Sodium hydroxide** (NaOH), 0.1 N standard: Dissolve 4.0 g NaOH in Type II water and dilute to 1 L. Standardize against an acid of known concentration.

5.8.5 **Methyl red indicator**, 0.1%: Dissolve 0.1 g in 99.9 mL of 95% ethanol and mix well.

5.9 Reagents for distillation option:

5.9.1 **Sodium chloride**, NaCl (acidified), 10%: Dissolve 100 g of NaCl (ammonium-free) in 900 mL of Type II water; mix well. Add approximately 0.42 mL of concentrated HCl to make the solution approximately 0.005 N.

5.9.2 **Sodium hydroxide** (NaOH), 1 N: Dissolve 40 g of NaOH in Type II water and dilute to 1 L.

5.9.3 **Boric acid** (H_3BO_3), 2% solution: Dissolve 20 g H_3BO_3 in 980 mL Type II water and mix well.

5.9.4 **Standard sulfuric acid** (H_2SO_4), 0.1 N: See Step 5.8.3.

5.9.5 **Bromocresol green-methyl red mixed indicator**: Triturate 0.1 g of bromocresol green with 2 mL 0.1 N NaOH in an agate mortar and add 95% ethyl alcohol to obtain a total volume of 100 mL. Triturate 0.1 g of methyl red with a few mL of 95% ethyl alcohol in an agate mortar. Add 3 mL of 0.1 N NaOH and dilute the solution to a volume of 100 mL with 95% ethyl alcohol. Mix 75 mL of the bromocresol green solution with 25 mL of the methyl red solution and dilute the mixture to 200 mL with 95% ethyl alcohol.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

7.0 PROCEDURE

7.1 Sieve a sample aliquot of the soil through a 2-mm screen and allow the sieved soil to air dry (at a temperature of $<60°C$). Place 10 g of the air-dried soil in a 500-mL Erlenmeyer flask and add 250 mL of neutral, 1 N NH_4OAc. (Use 25 g of soil if the exchange capacity is very low, e.g., 3-5 meq per 100 g.) Shake the flask thoroughly and allow it to stand overnight.

7.2 Filter the soil with light suction using a 55-mm Buchner funnel or equivalent. Do not allow the soil to become dry and cracked.

7.3 Leach the soil with the neutral NH_4OAc reagent until no test for calcium can be obtained in the effluent solution. (For the calcium test, add a few drops each of 1 N NH_4Cl and 10% ammonium oxalate, dilute NH_4OH to 10 mL of the leachate in a test tube, and heat the solution to near the boiling point. The presence of calcium is indicated by a white precipitate or turbidity.)

7.4 Then leach the soil four times with neutral 1 N NH_4Cl and once with 0.25 N NH_4Cl.

7.5 Wash out the electrolyte with 150 to 200 mL of 99% isopropyl alcohol. When the test for chloride in the leachate (use 0.10 $AgNO_3$) becomes negligible, allow the soil to drain thoroughly.

7.6 Determine the adsorbed NH_4 either by the aeration method (Paragraph 7.7) or by the acid-NaCl method (Paragraph 7.8).

7.7 Aeration method:

7.7.1 Place an excess of 0.1 N standard H_2SO_4 in the 500-mL Erlenmeyer flask on the aeration apparatus (50 mL is an ample quantity for most soils) and add 10 drops of methyl red indicator and enough distilled water to make the total volume about 100 mL.

7.7.2 Attach the flask to the apparatus. Then transfer the ammonium-saturated sample of soil (from Paragraph 7.5) quantitatively to the 800-mL Kjeldahl flask located in the flow line just before the Erlenmeyer flask with the standard acid. Use a rubber policeman and a stream of distilled water from a wash bottle, as needed, to complete the transfer.

7.7.3 Add 150 mL Na_2CO_3 solution and a few drops of paraffin oil and attach the flask to the apparatus.

7.7.4 Apply suction to the outflow end of the apparatus and adjust the rate of flow to 450 to 500 liters of air per hr. Continue the aeration for 17 hr.

7.7.5 Shut off the suction and remove the flask. Titrate the residual acid in the absorption solutions with standard 0.1 N NaOH from the original red color through orange to yellow at the end point. From the titration values obtained with the soil and blank solutions, calculate the content of adsorbed ammonium in milligram equivalents per 100 g soil.

7.8 Acid-NaCl method:

7.8.1 Leach the ammonium-saturated soil from Paragraph 7.5 with 10% acidified NaCl until 225 mL have passed through the sample. Add small portions at a time, allowing each portion to pass through the sample before adding the next portion.

7.8.2 Transfer the leachate quantitatively to an 800-mL Kjeldahl flask, add 25 mL of 1 N NaOH, and distill 60 mL of the solution into 50 mL of 2% H_3BO_3.

7.8.3 Add 10 drops of bromocresol green-methyl red mixed indicator and titrate the boric acid solution with standard 0.1 N H_2SO_4. The color change is from bluish green through bluish purple to pink at the end point. Run blanks on the reagents. Correct the titration figure for the blanks and calculate the milliequivalents of ammonium in 100 g of soil.

7.8.4 Results should be reported as "determined with ammonium acetate" at pH 7.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

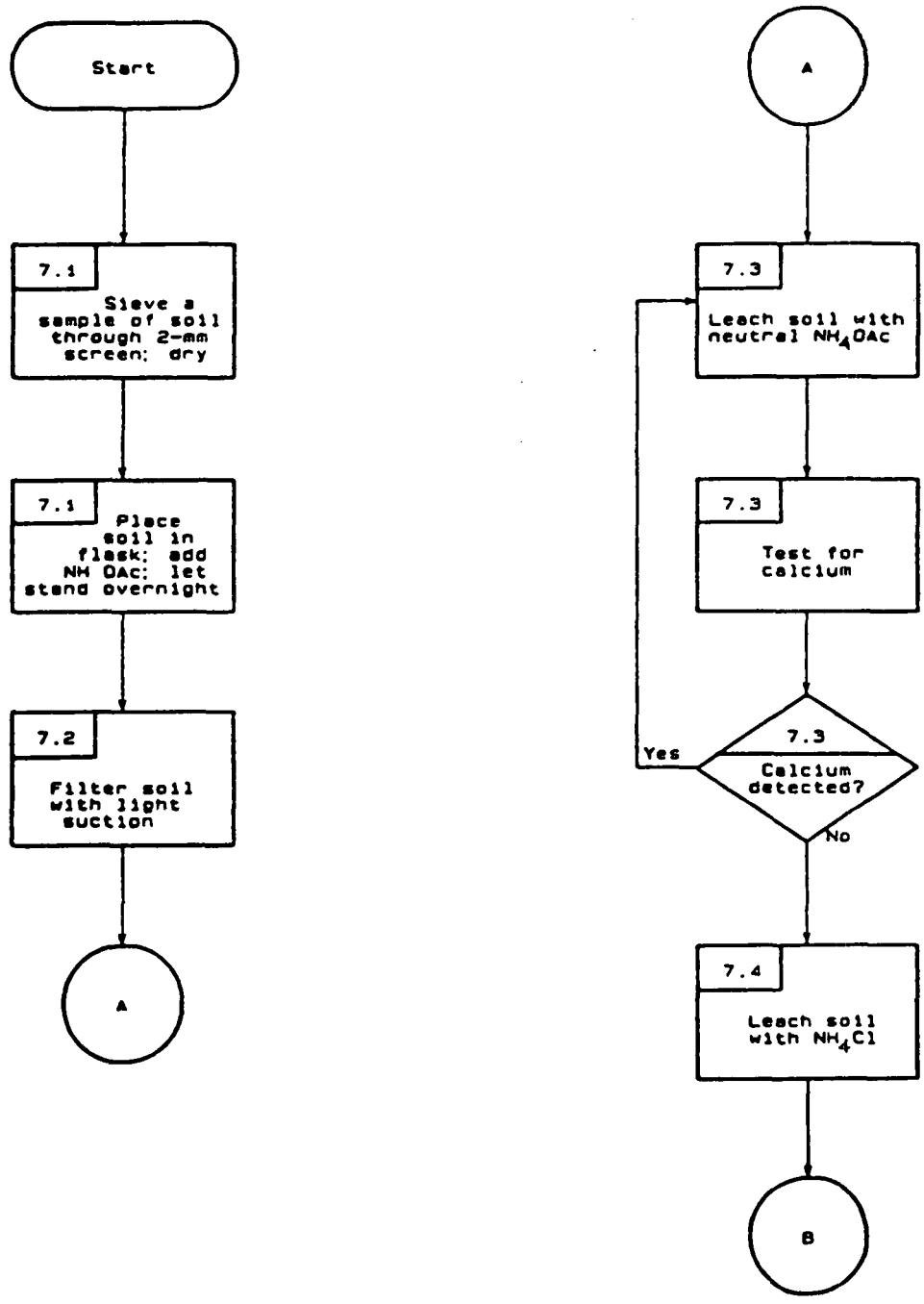
8.3 Material of known cation-exchange capacity must be routinely analyzed.

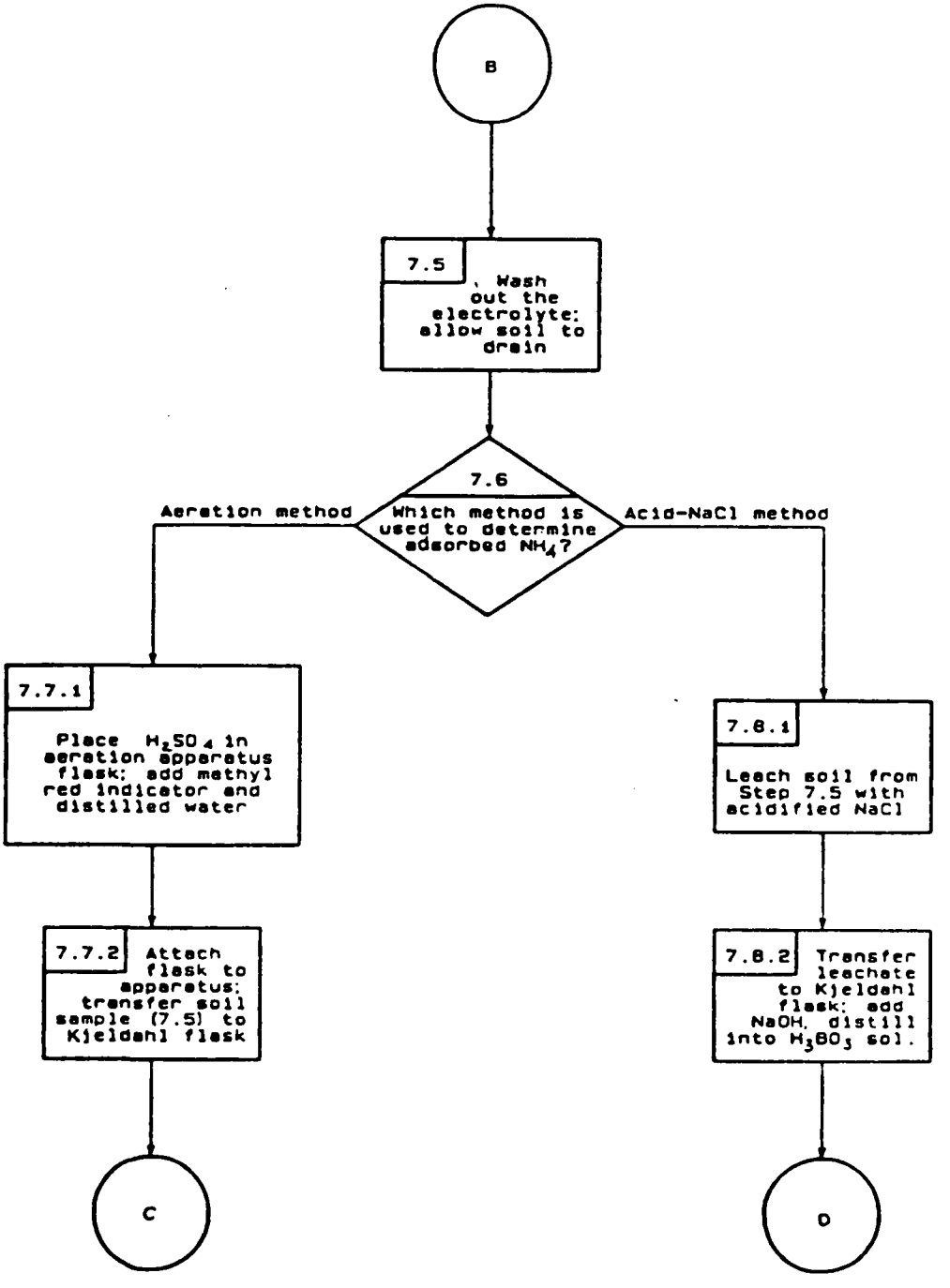
9.0 METHOD PERFORMANCE

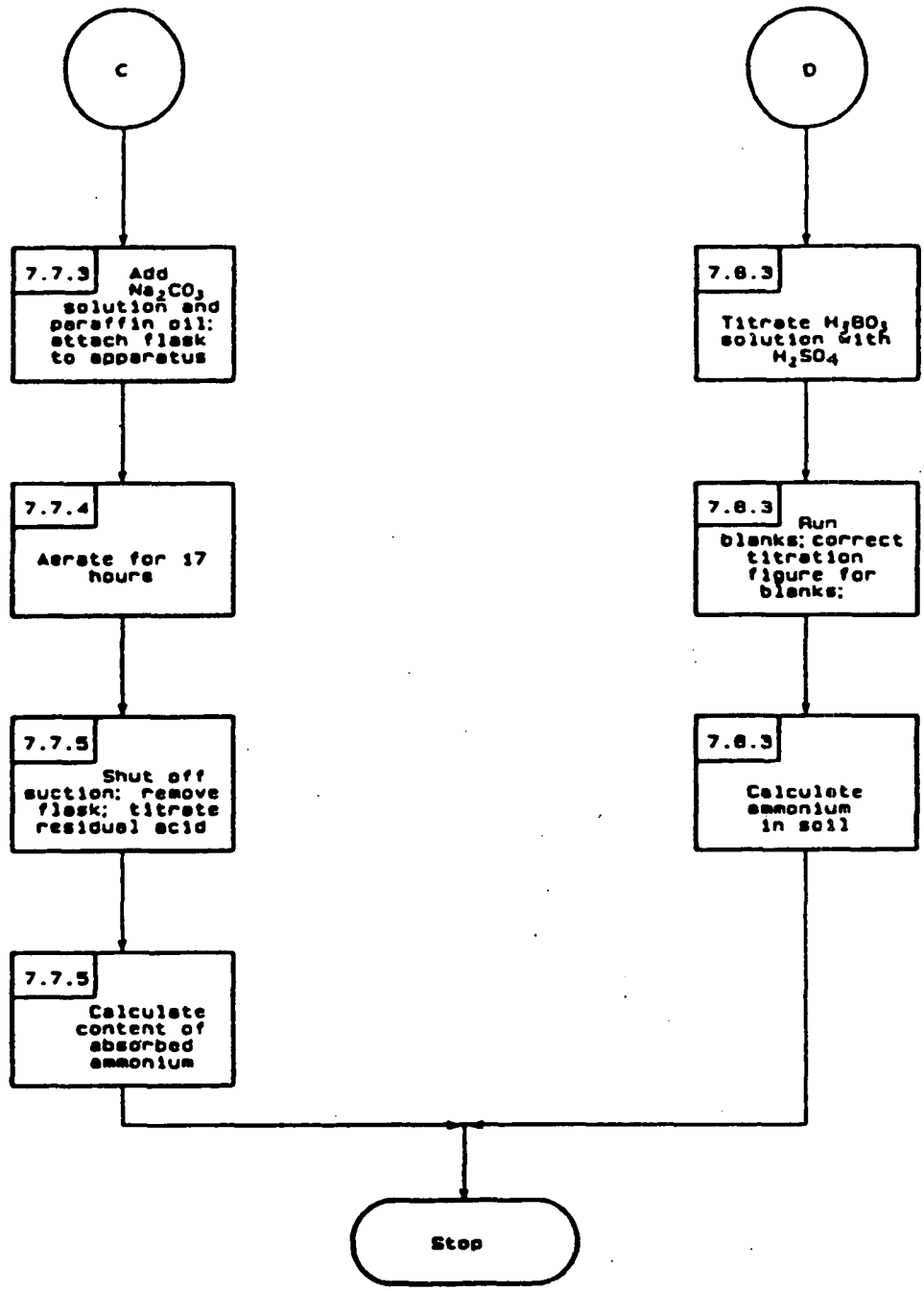
9.1 No data provided.

10.0 REFERENCES

1. This method is based on Chapman, H.D., "Cation-exchange Capacity," pp. 891-900, in C.A. Black (ed.), Method of Soil Analysis, Part 2: Chemical and Microbiological Properties, Am. Soc. Agron., Madison, Wisconsin (1965).


Start
7.1
Sieve a sample of soil through 2-mm screen; dry
7.1
Place soil in flask; add NH OAc; let stand overnight
7.2
Filter soil with light suction
A
A
7.3
Leach soil with neutral NH4OAc
7.3
Test for calcium
7.3
Calcium detected?
Yes
No
7.4
Leach soil with NH4Cl
B


B
7.5
Wash out the electrolyte; allow soil to drain
7.6
Which method is used to determine adsorbed NH_4?
Aeration method
Acid-NaCl method
7.7.1
Place H_2SO_4 in aeration apparatus flask; add methyl red indicator and distilled water
7.7.2
Attach flask to apparatus; transfer soil sample (7.5) to Kjeldahl flask
C
7.8.1
Leach soil from Step 7.5 with acidified NaCl
7.8.2
Transfer leachate to Kjeldahl flask; add NaOH, distill into H_3BO_3 sol.
D


C
D
7.7.3 Add Na_2CO_3 solution and paraffin oil: attach flask to apparatus
7.7.4 Aerate for 17 hours
7.7.5 Shut off suction: remove flask; titrate residual acid
7.7.5 Calculate content of absorbed ammonium
7.8.3 Titrate H_3BO_3 solution with H_2SO_4
7.8.3 Run blanks; correct titration figure for blanks;
7.8.3 Calculate ammonium in soil
Stop

METHOD 9081

CATION-EXCHANGE CAPACITY OF SOILS (SODIUM ACETATE)

1.0 SCOPE AND APPLICATION

1.1 Method 9081 is applicable to most soils, including calcareous and noncalcareous soils. The method of cation-exchange capacity by summation (Chapman, 1965, p. 900; see Paragraph 10.1) should be employed for distinctly acid soils.

2.0 SUMMARY OF METHOD

2.1 The soil sample is mixed with an excess of sodium acetate solution, resulting in an exchange of the added sodium cations for the matrix cations. Subsequently, the sample is washed with isopropyl alcohol. An ammonium acetate solution is then added, which replaces the adsorbed sodium with ammonium. The concentration of displaced sodium is then determined by atomic absorption, emission spectroscopy, or an equivalent means.

3.0 INTERFERENCES

3.1 Interferences can occur during analysis of the extract for sodium content. Thoroughly investigate the chosen analytical method for potential interferences.

4.0 APPARATUS AND MATERIALS

4.1 Centrifuge tube and stopper: 50-mL, round-bottom, narrow neck.

4.2 Mechanical shaker.

4.3 Volumetric flask: 100-mL.

5.0 REAGENTS

5.1 Sodium acetate (NaOAc), 1.0 N: Dissolve 136 g of $NaC_2H_2O_2 \cdot 3H_2O$ in water and dilute it to 1,000 mL. The pH of this solution should be 8.2. If needed, add a few drops of acetic acid or NaOH solution to bring the reaction of the solution to pH 8.2.

5.2 Ammonium acetate (NH_4OAc), 1 N: Dilute 114 mL of glacial acetic acid (99.5%) with water to a volume of approximately 1 liter. Then add 138 mL of concentrated ammonium hydroxide (NH_4OH) and add water to obtain a volume of about 1,980 mL. Check the pH of the resulting solution, add more NH_4OH, as needed, to obtain a pH of 7, and dilute the solution to a volume of 2 liters with water.

5.3 Isopropyl alcohol: 99%.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

7.0 PROCEDURE

7.1 Weigh 4 g of medium- or fine-textured soil or 6 g of coarse-textured soil and transfer the sample to a 50-mL, round-bottom, narrow-neck centrifuge tube. (A fine soil has >50% of the particles <0.074 mm, medium soil has >50% >0.425 mm, while a coarse soil has more than 50% of its particles >2 mm.

7.2 Add 33 mL of 1.0 N NaOAc solution, stopper the tube, shake it in a mechanical shaker for 5 min, and centrifuge it until the supernatant liquid is clear.

7.3 Decant the liquid, and repeat Paragraph 7.2 three more times.

7.4 Add 33 mL of 99% isopropyl alcohol, stopper the tube, shake it in a mechanical shaker for 5 min, and centrifuge it until the supernatant liquid is clear.

7.5 Repeat the procedure described in Paragraph 7.4 two more times.

7.6 Add 33 mL of NH_4OAc solution, stopper the tube, shake it in a mechanical shaker for 5 min, and centrifuge it until the supernatant liquid is clear. Decant the washing into a 100-mL volumetric flask.

7.7 Repeat the procedure described in Paragraph 7.6 two more times.

7.8 Dilute the combined washing to the 100-mL mark with ammonium acetate solution and determine the sodium concentration by atomic absorption, emission spectroscopy, or an equivalent method.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

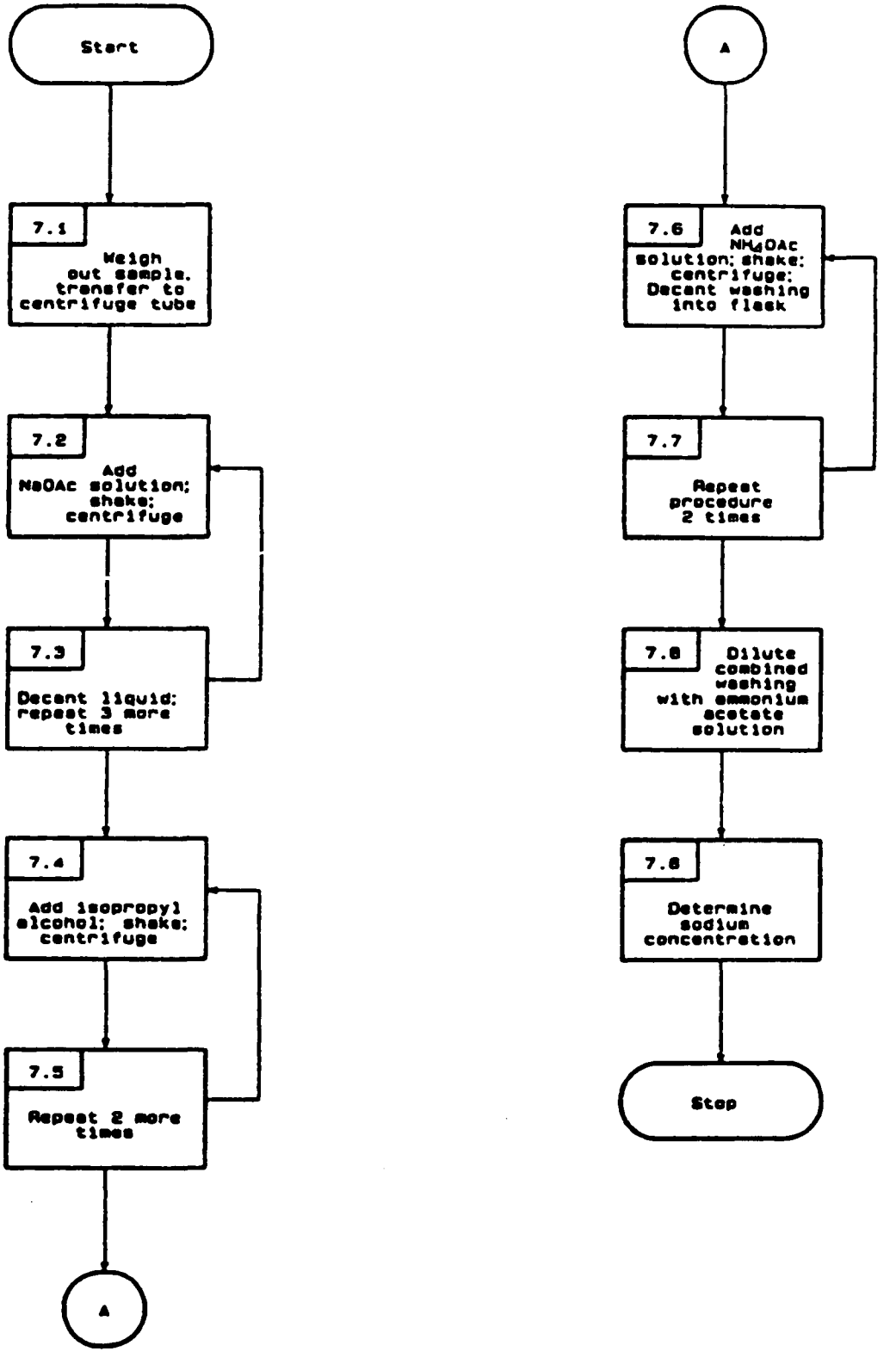
8.3 Materials of known cation-exchange capacity must be routinely analyzed.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

10.1 This method is based on Chapman, H.D., "Cation-exchange Capacity," pp. 891-900, in C.A. Black (ed.), Method of Soil Analysis, Part 2: Chemical and Microbiological Properties, Am. Soc. Agron., Madison, Wisconsin (1965).


Start
7.1
Weigh out sample, transfer to centrifuge tube
7.2
Add NaOAc solution; shake; centrifuge
7.3
Decant liquid; repeat 3 more times
7.4
Add isopropyl alcohol; shake; centrifuge
7.5
Repeat 2 more times
A
A
7.6
Add NH4OAc solution; shake; centrifuge; Decant washing into flask
7.7
Repeat procedure 2 times
7.8
Dilute combined washing with ammonium acetate solution
7.8
Determine sodium concentration
Stop

METHOD 9090A

COMPATIBILITY TEST FOR WASTES AND MEMBRANE LINERS

1.0 SCOPE AND APPLICATION

1.1 Method 9090 is intended for use in determining the effects of chemicals in a surface impoundment, waste pile, or landfill on the physical properties of flexible membrane liner (FML) materials intended to contain them. Data from these tests will assist in deciding whether a given liner material is acceptable for the intended application.

2.0 SUMMARY OF METHOD

2.1 In order to estimate waste/liner compatibility, the liner material is immersed in the chemical environment for minimum periods of 120 days at room temperature (23 $\pm$ 2°C) and at 50 $\pm$ 2°C. In cases where the FML will be used in a chemical environment at elevated temperatures, the immersion testing shall be run at the elevated temperatures if they are expected to be higher than 50°C. Whenever possible, the use of longer exposure times is recommended. Comparison of measurements of the membrane's physical properties, taken periodically before and after contact with the waste fluid, is used to estimate the compatibility of the liner with the waste over time.

3.0 INTERFERENCES (Not Applicable)

4.0 APPARATUS AND MATERIALS

NOTE: In general, the following definitions will be used in this method:

1. Sample - a representative piece of the liner material proposed for use that is of sufficient size to allow for the removal of all necessary specimens.

2. Specimen - a piece of material, cut from a sample, appropriately shaped and prepared so that it is ready to use for a test.

4.1 Exposure tank - Of a size sufficient to contain the samples, with provisions for supporting the samples so that they do not touch the bottom or sides of the tank or each other, and for stirring the liquid in the tank. The tank should be compatible with the waste fluid and impermeable to any of the constituents they are intended to contain. The tank shall be equipped with a means for maintaining the solution at room temperature (23 $\pm$ 2°C) and 50 $\pm$ 2°C and for preventing evaporation of the solution (e.g., use a cover equipped with a reflux condenser, or seal the tank with a Teflon gasket and use an airtight cover). Both sides of the liner material shall be exposed to the chemical environment. The pressure inside the tank must be the same as that outside the tank. If the liner has a side that (1) is not exposed to the waste in actual use and (2) is not designed to withstand exposure to the chemical environment, then such a liner may be treated with only the barrier surface exposed.

4.2 Stress-strain machine suitable for measuring elongation, tensile strength, tear resistance, puncture resistance, modulus of elasticity, and ply adhesion.

4.3 Jig for testing puncture resistance for use with FTMS 101C, Method 2065.

4.4 Liner sample labels and holders made of materials known to be resistant to the specific wastes.

4.5 Oven at 105 ± 2°C.

4.6 Dial micrometer.

4.7 Analytical balance.

4.8 Apparatus for determining extractable content of liner materials.

NOTE: A minimum quantity of representative waste fluid necessary to conduct this test has not been specified in this method because the amount will vary depending upon the waste composition and the type of liner material. For example, certain organic waste constituents, if present in the representative waste fluid, can be absorbed by the liner material, thereby changing the concentration of the chemicals in the waste. This change in waste composition may require the waste fluid to be replaced at least monthly in order to maintain representative conditions in the waste fluid. The amount of waste fluid necessary to maintain representative waste conditions will depend on factors such as the volume of constituents absorbed by the specific liner material and the concentration of the chemical constituents in the waste.

5.0 REAGENTS (Not Applicable)

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 For information on what constitutes a representative sample of the waste fluid, refer to the following guidance document:

Permit Applicants' Guidance Manual for Hazardous Waste Land Treatment, Storage, and Disposal Facilities; Final Draft; Chap. 5, pp. 15-17; Chap. 6, pp. 18-21; and Chap. 8, pp. 13-16, May 1984.

7.0 PROCEDURE

7.1 Obtain a representative sample of the waste fluid. If a waste sample is received in more than one container, blend thoroughly. Note any signs of stratification. If stratification exists, liner samples must be placed in each of the phases. In cases where the waste fluid is expected to stratify and the phases cannot be separated, the number of immersed samples per exposure period can be increased (e.g., if the waste fluid has two phases, then 2 samples per exposure period are needed) so that test samples exposed at each level of the waste can be tested. If the waste to be contained in the land disposal unit is in solid form, generate a synthetic leachate (see Step 7.9.1).

7.2 Perform the following tests on unexposed samples of the polymeric membrane liner material at 23 ± 2°C (see Steps 7.9.2 and 7.9.3 below for additional tests suggested for specific circumstances). Tests for tear resistance and tensile properties are to be performed according to the protocols referenced in Table 1. See Figure 1 for cutting patterns for nonreinforced liners, Figure 2 for cutting patterns for reinforced liners, and Figure 3 for cutting patterns for semicrystalline liners. (Table 2, at the end of this method, gives characteristics of various polymeric liner materials.)

1. Tear resistance, machine and transverse directions, three specimens each direction for nonreinforced liner materials only. See Table 1 for appropriate test method, the recommended test speed, and the values to be reported.

2. Puncture resistance, two specimens, FTMS 101C, Method 2065. See Figure 1, 2, or 3, as applicable, for sample cutting patterns.

3. Tensile properties, machine and transverse directions, three tensile specimens in each direction. See Table 1 for appropriate test method, the recommended test speed, and the values to be reported. See Figure 4 for tensile dumbbell cutting pattern dimensions for nonreinforced liner samples.

4. Hardness, three specimens, Duro A (Duro D if Duro A reading is greater than 80), ASTM D2240. The hardness specimen thickness for Duro A is 1/4 in., and for Duro D it is 1/8 in. The specimen dimensions are 1 in. by 1 in.

5. Elongation at break. This test is to be performed only on membrane materials that do not have a fabric or other nonelastomeric support as part of the liner.

6. Modulus of elasticity, machine and transverse directions, two specimens each direction for semicrystalline liner materials only, ASTM D882 modified Method A (see Table 1).

7. Volatiles content, SW 870, Appendix III-D.

8. Extractables content, SW 870, Appendix III-E.

9. Specific gravity, three specimens, ASTM D792 Method A.

10. Ply adhesion, machine and transverse directions, two specimens each direction for fabric reinforced liner materials only, ASTM D413 Machine Method, Type A -- 180 degree peel.

11. Hydrostatic resistance test, ASTM D751 Method A, Procedure 1.

7.3 For each test condition, cut five pieces of the lining material of a size to fit the sample holder, or at least 8 in. by 10 in. The fifth sample is an extra sample. Inspect all samples for flaws and discard unsatisfactory ones. Liner materials with fabric reinforcement require close inspection to ensure that threads of the samples are evenly spaced and straight at 90°. Samples containing a fiber scrim support may be flood-coated along the exposed

edges with a solution recommended by the liner manufacturer, or another procedure should be used to prevent the scrim from being directly exposed. The flood-coating solution will typically contain 5-15% solids dissolved in a solvent. The solids content can be the liner formula or the base polymer.

Measure the following:

1. Gauge thickness, in. -- average of the four corners.

2. Mass, lb. -- to one-hundredth of a lb.

3. Length, in. -- average of the lengths of the two sides plus the length measured through the liner center.

4. Width, in. -- average of the widths of the two ends plus the width measured through the liner center.

NOTE: Do not cut these liner samples into the test specimen shapes shown in Figure 1, 2, or 3 at this time. Test specimens will be cut as specified in Step 7.7, after exposure to the waste fluid.

7.4 Label the liner samples (e.g., notch or use metal staples to identify the sample) and hang in the waste fluid by a wire hanger or a weight. Different liner materials should be immersed in separate tanks to avoid exchange of plasticizers and soluble constituents when plasticized membranes are being tested. Expose the liner samples to the stirred waste fluid held at room temperature and at 50 $\pm$ 2°C.

7.5 At the end of 30, 60, 90, and 120 days of exposure, remove one liner sample from each test condition to determine the membrane's physical properties (see Steps 7.6 and 7.7). Allow the liner sample to cool in the waste fluid until the waste fluid has a stable room temperature. Wipe off as much waste as possible and rinse briefly with water. Place wet sample in a labeled polyethylene bag or aluminum foil to prevent the sample from drying out. The liner sample should be tested as soon as possible after removal from the waste fluid at room temperature, but in no case later than 24 hours after removal.

7.6 To test the immersed sample, wipe off any remaining waste and rinse with deionized water. Blot sample dry and measure the following as in Step 7.3:

1. Gauge thickness, in.

2. Mass, lb.

3. Length, in.

4. Width, in.

7.7 Perform the following tests on the exposed samples (see Steps 7.9.2 and 7.9.3 below for additional tests suggested for specific circumstances). Tests for tear resistance and tensile properties are to be performed according to the protocols referenced in Table 1. Die-cut test specimens following suggested cutting patterns. See Figure 1 for cutting patterns for nonreinforced

liners, Figure 2 for cutting patterns for reinforced liners, and Figure 3 for semicrystalline liners.

1. Tear resistance, machine and transverse directions, three specimens each direction for materials without fabric reinforcement. See Table 1 for appropriate test method, the recommended test specimen and speed of test, and the values to be reported.

2. Puncture resistance, two specimens, FTMS 101C, Method 2065. See Figure 1, 2, or 3, as applicable, for sample cutting patterns.

3. Tensile properties, machine and transverse directions, three specimens each direction. See Table 1 for appropriate test method, the recommended test specimen and speed of test, and the values to be reported. See Figure 4 for tensile dumbbell cutting pattern dimensions for nonreinforced liner samples.

4. Hardness, three specimens, Duro A (Duro D if Duro A reading is greater than 80), ASTM 2240. The hardness specimen thickness for Duro A is 1/4 in., and for Duro D is 1/8 in. The specimen dimensions are 1 in. by 1 in.

5. Elongation at break. This test is to be performed only on membrane materials that do not have a fabric or other nonelastomeric support as part of the liner.

6. Modulus of elasticity, machine and transverse directions, two specimens each direction for semicrystalline liner materials only, ASTM D882 modified Method A (see Table 1).

7. Volatiles content, SW 870, Appendix III-D.

8. Extractables content, SW 870, Appendix III-E.

9. Ply adhesion, machine and transverse directions, two specimens each direction for fabric reinforced liner materials only, ASTM D413 Machine Method, Type A -- 180 degree peel.

10. Hydrostatic resistance test, ASTM D751 Method A, Procedure 1.

7.8 Results and reporting

7.8.1 Plot the curve for each property over the time period 0 to 120 days and display the spread in data points.

7.8.2 Report all raw, tabulated, and plotted data. Recommended methods for collecting and presenting information are described in the documents listed under Step 6.1 and in related agency guidance manuals.

7.8.3 Summarize the raw test results as follows:

1. Percent change in thickness.

2. Percent change in mass.

3. Percent change in area (provide length and width dimensions).

4. Percent retention of physical properties.

5. Change, in points, of hardness reading.

6. The modulus of elasticity calculated in pounds-force per square inch.

7. Percent volatiles of unexposed and exposed liner material.

8. Percent extractables of unexposed and exposed liner material.

9. The adhesion value, determined in accordance with ASTM D413, Step 12.2.

10. The pressure and time elapsed at the first appearance of water through the flexible membrane liner for the hydrostatic resistance test.

7.9 The following additional procedures are suggested in specific situations:

7.9.1 For the generation of a synthetic leachate, the Agency suggests the use of the Toxicity Characteristic Leaching Procedure (TCLP) that was finalized in the Federal Register on June 29, 1990, Vol. 55, No. 126, p. 26986.

7.9.2 For semicrystalline membrane liners, the Agency suggests the determination of the potential for environmental stress cracking. The test that can be used to make this determination is either ASTM D1693 or the National Institute of Standards and Technology Constant Tensile Load. The evaluation of the results should be provided by an expert in this field.

7.9.3 For field seams, the Agency suggests the determination of seam strength in shear and peel modes. To determine seam strength in peel mode, the test ASTM D413 can be used. To determine seam strength in shear mode for nonreinforced FMLs, the test ASTM D3083 can be used, and for reinforced FMLs, the test ASTM D751, Grab Method, can be used at a speed of 12 in. per minute. The evaluation of the results should be provided by an expert in this field.

8.0 QUALITY CONTROL

8.1 Determine the mechanical properties of identical nonimmersed and immersed liner samples in accordance with the standard methods for the specific physical property test. Conduct mechanical property tests on nonimmersed and immersed liner samples prepared from the same sample or lot of material in the same manner and run under identical conditions. Test liner samples immediately after they are removed from the room temperature test solution.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. None required.

Table 1. Physical testing of exposed membranes in liner-waste liquid compatibility test

Type of compound and construction	Crosslinked or vulcanized	Thermoplastic	Semicrystalline	Fabric-reinforced[a]
Tensile properties method	ASTM D412	ASTM D638	ASTM D638	ASTM D751, Method B
Type of specimen	Dumbbell[b]	Dumbbell[b]	Dumbbell[b]	1-in. wide strip and 2-in. jaw separation
Number of specimens	3 in each direction	3 in each direction	3 in each direction	3 in each direction
Speed of test	20 ipm	20 ipm	2 ipm	12 ipm
Values to be reported	Tensile strength, psi Elongation at break, % Tensile set after break, % Stress at 100 and 200% elongation, psi	Tensile strength, psi Elongation at break, % Tensile set after break, % Stress at 100 and 200% elongation, psi	Tensile strength at yield, psi Elongation at yield, % Tensile set at break, psi Elongation at break, psi Tensile set after break, % Stress at 100 and 200% elongation, psi	Tensile at fabric break, ppi Elongation at fabric break, % Tensile at ultimate break, ppi Elongation at ultimate break, ppi Tensile set after break, % Stress at 100 and 200% elongation, psi
Modulus of elasticity method	c	c	ASTM D882, Method A	c
Type of specimen	—	—	Strip: 0.5 in. wide and 6. in long at a 2 in. jaw separation	—
Number of specimens	—	—	2 in each direction	—
Speed of test	—	—	0.2 ipm	—
Values reported	—	—	Greatest slope of initial stress - strain curve, psi	—
Tear resistance method	ASTM D624	ASTM 1004	ASTM D1004	d
Type of specimen	Die C	e	e	—
Number of specimens	3 in each direction	3 in each direction	2 in each direction	—
Speed of test	20 ipm	20 ipm	2 ipm	—
Values reported	Stress, ppi	Stress, ppi	Maximum stress, ppi	—
Puncture resistance method	FTMS 101C, Method 2065	FTMS 101C, Method 2065	FTMS 101C, Method 2065	FTMS 101C, Method 2065
Type of specimen	2 in. square	2 in. square	2 in. square	2 in. square
Number of specimens	2	2	2	2
Speed of test	20 ipm	20 ipm	20 ipm	20 ipm
Values reported	Gage, mil Stress, l[b] Elongation, in.	Gage, mil Stress, l[b] Elongation, in.	Gage, mil Stress, l[b] Elongation, in.	Gage, mil Stress, l[b] Elongation, in.

[a]Can be thermoplastic, crosslinked, or vulcanized membrane.
[b]See Figure 4.
[c]Not performed on this material.
[d]No tear resistance test is recommended for fabric-reinforced sheetings in the immersion study.
[e]Same as ASTM D624, Die C.

TABLE 2.
POLYMERS USED IN FLEXIBLE MEMBRANE LINERS

Thermoplastic Materials (TP)

CPE (Chlorinated polyethylene)[a]

A family of polymers produced by a chemical reaction of chlorine on polyethylene. The resulting thermoplastic elastomers contain 25 to 45% chlorine by weight and 0 to 25% crystallinity.

CSPE (Chlorosulfonated polyethylene)[a]

A family of polymers that are produced by the reaction of polyethylene with chlorine and sulfur dioxide, usually containing 25 to 43% chlorine and 1.0 to 1.4% sulfur. Chlorosulfonated polyethylene is also known as hypalon.

EIA (Ethylene interpolymer alloy)[a]

A blend of EVA and polyvinyl chloride resulting in a thermoplastic elastomer.

PVC (Polyvinyl chloride)[a]

A synthetic thermoplastic polymer made by polymerizing vinyl chloride monomer or vinyl chloride/vinyl acetate monomers. Normally rigid and containing 50% of plasticizers.

PVC-CPE (Polyvinyl chloride - chlorinated polyethylene alloy)[a]

A blend of polyvinyl chloride and chlorinated polyethylene.

TN-PVC (Thermoplastic nitrile-polyvinyl chloride)[a]

An alloy of thermoplastic unvulcanized nitrile rubber and polyvinyl chloride.

Vulcanized Materials (XL)

Butyl rubber[a]

A synthetic rubber based on isobutylene and a small amount of isoprene to provide sites for vulcanization.

---

aAlso supplied reinforced with fabric.

TABLE 2. (Continued)

EPDM (Ethylene propylene diene monomer)[a,b]

A synthetic elastomer based on ethylene, propylene, and a small amount of nonconjugated diene to provide sites for vulcanization.

CM (Cross-linked chlorinated polyethylene)

No definition available by EPA.

CO, ECO (Epichlorohydrin polymers)[a]

Synthetic rubber, including two epichlorohydrin-based elastomers that are saturated, high-molecular-weight aliphatic polyethers with chloromethyl side chains. The two types include homopolymer (CO) and a copolymer of epichlorohydrin and ethylene oxide (ECO).

CR (Polychloroprene)[a]

Generic name for a synthetic rubber based primarily on chlorobutadiene. Polychloroprene is also known as neoprene.

Semicrystalline Materials (CX)

HDPE - (High-density polyethylene)

A polymer prepared by the low-pressure polymerization of ethylene as the principal monomer.

HDPE - A (High-density polyethylene/rubber alloy)

A blend of high-density polyethylene and rubber.

LLDPE (Liner low-density polyethylene)

A low-density polyethylene produced by the copolymerization of ethylene with various alpha olefins in the presence of suitable catalysts.

PEL (Polyester elastomer)

A segmented thermoplastic copolyester elastomer containing recurring long-chain ester units derived from dicarboxylic acids and long-chain glycols and short-chain ester units derived from dicarboxylic acids and low-molecular-weight diols.

[a]Also supplied reinforced with fabric.
[b]Also supplied as a thermoplastic.

TABLE 2. (Continued)

PE-EP-A (Polyethylene ethylene/propylene alloy)

A blend of polyethylene and ethylene and propylene polymer resulting in a thermoplastic elastomer.

T-EPDM (Thermoplastic EPDM)

An ethylene-propylene diene monomer blend resulting in a thermoplastic elastomer.

FIGURE 1. SUGGESTED PATTERN FOR CUTTING TEST SPECIMENS FROM NONREINFORCED CROSSLINKED OR THERMOPLASTIC IMMERSED LINER SAMPLES.

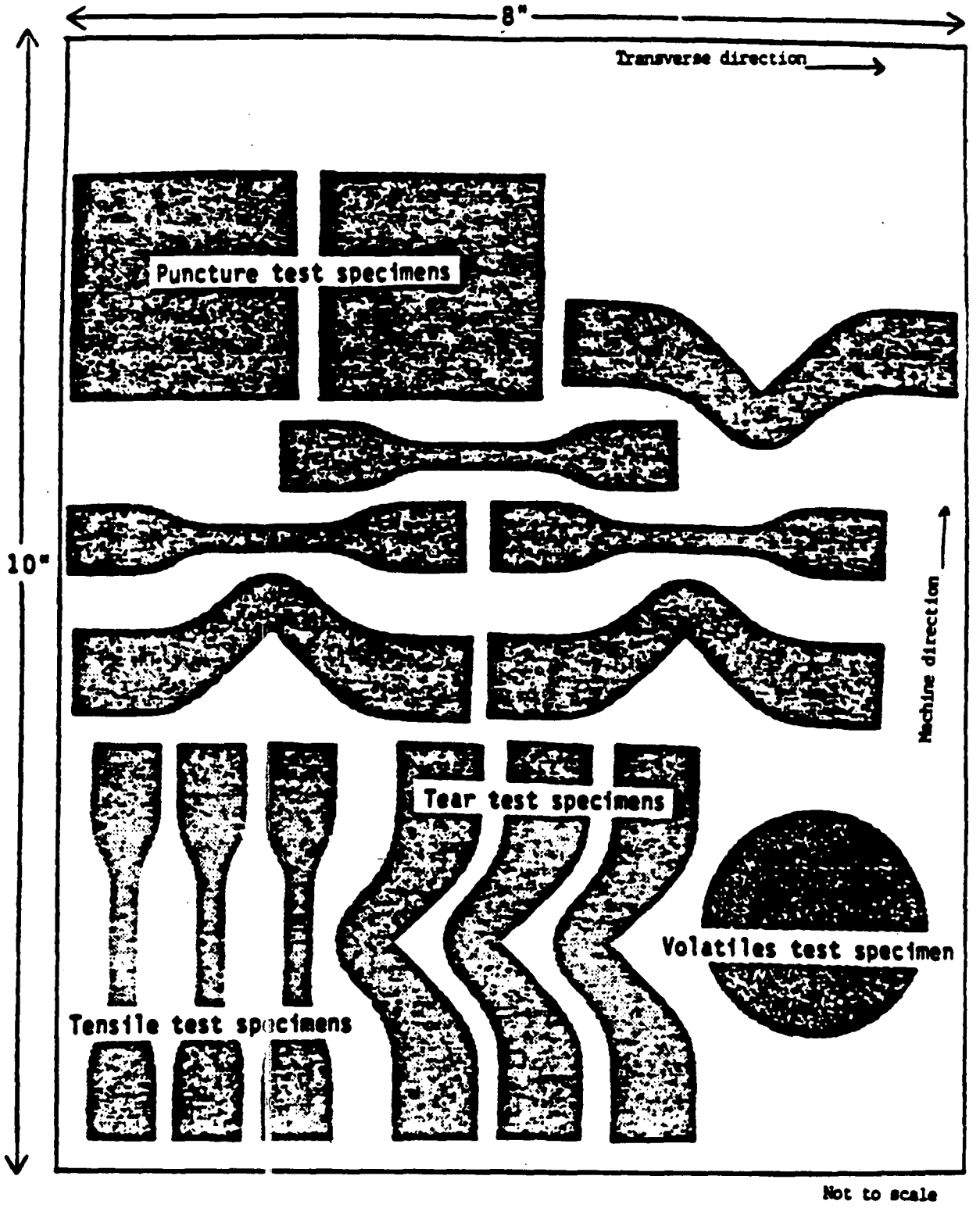


FIGURE 2. SUGGESTED PATTERN FOR CUTTING TEST SPECIMENS FROM FABRIC REINFORCED IMMERSED LINER SAMPLES.

NOTE: TO AVOID EDGE EFFECTS, CUT SPECIMENS 1/8 - 1/4 INCH IN FROM EDGE OF IMMERSED SAMPLE.

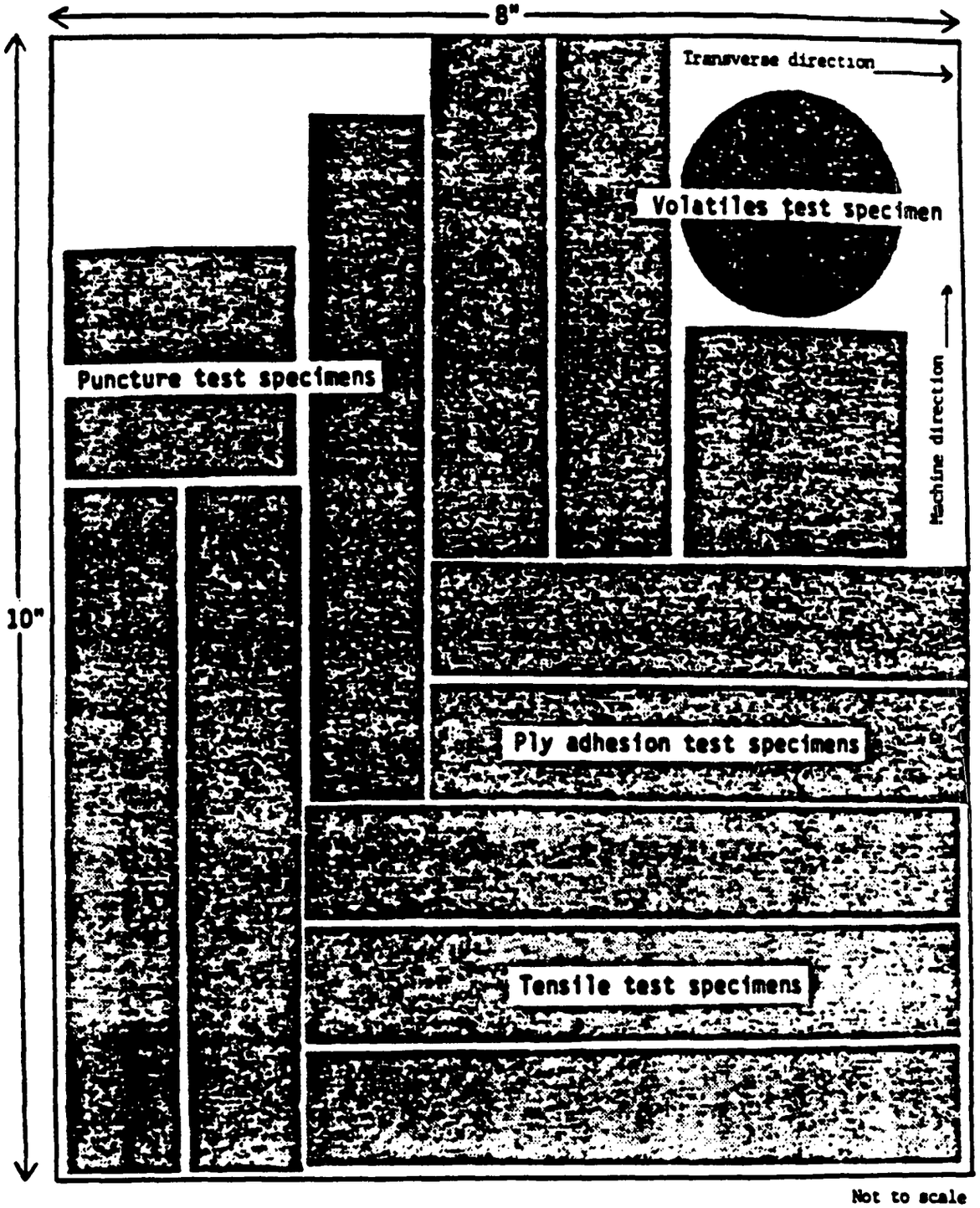


FIGURE 3. SUGGESTED PATTERN FOR CUTTING TEST SPECIMENS FROM SEMICRYSTALLINE IMMERSED LINER SAMPLES.

NOTE: TO AVOID EDGE EFFECTS, CUT SPECIMENS 1/8 TO 1/4 INCH IN FROM EDGE OF IMMERSED SAMPLE.

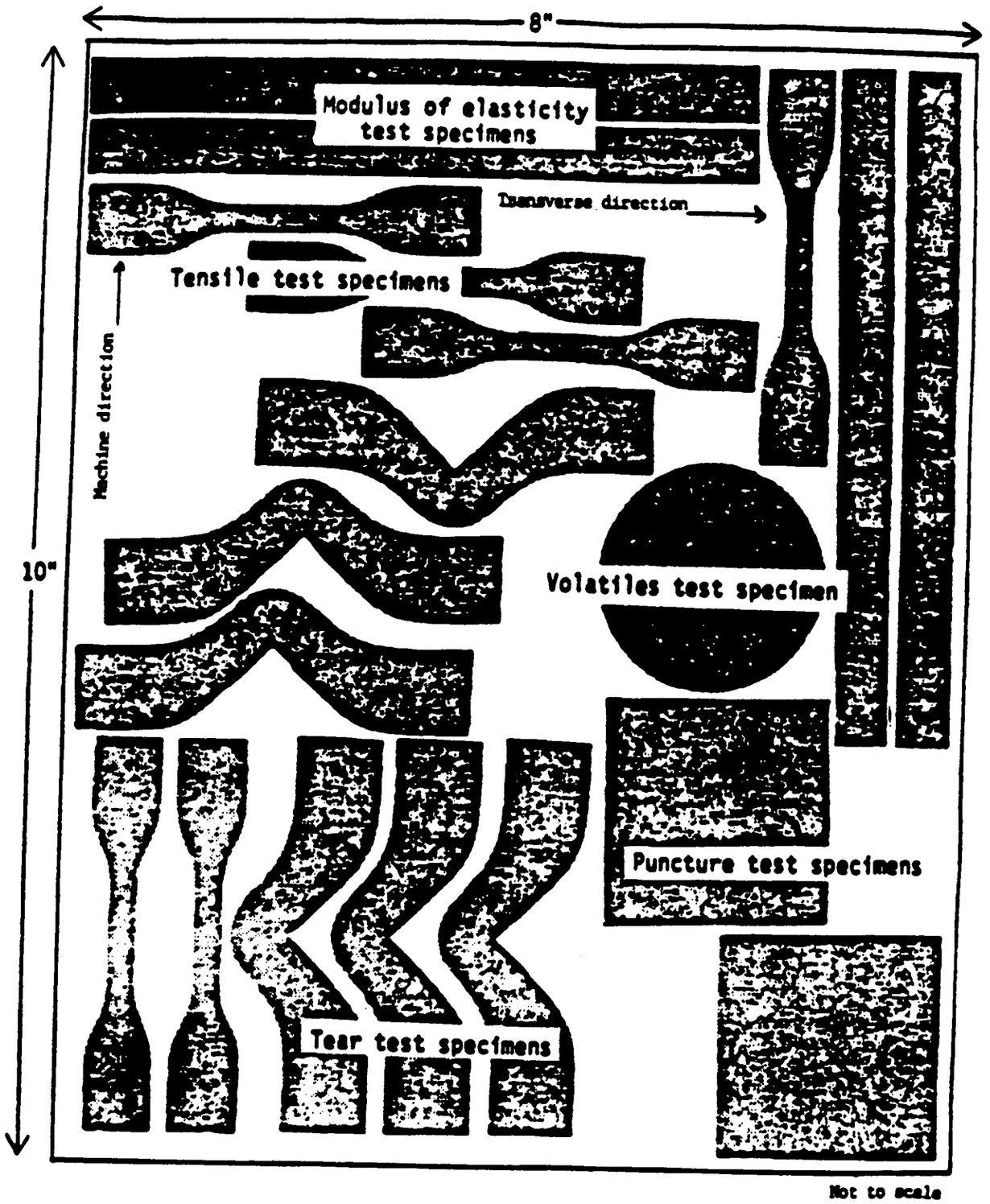
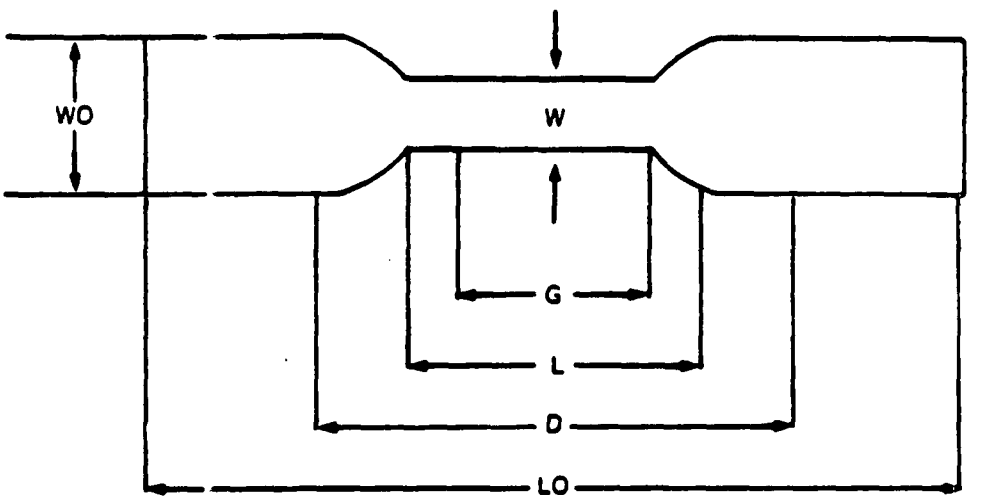
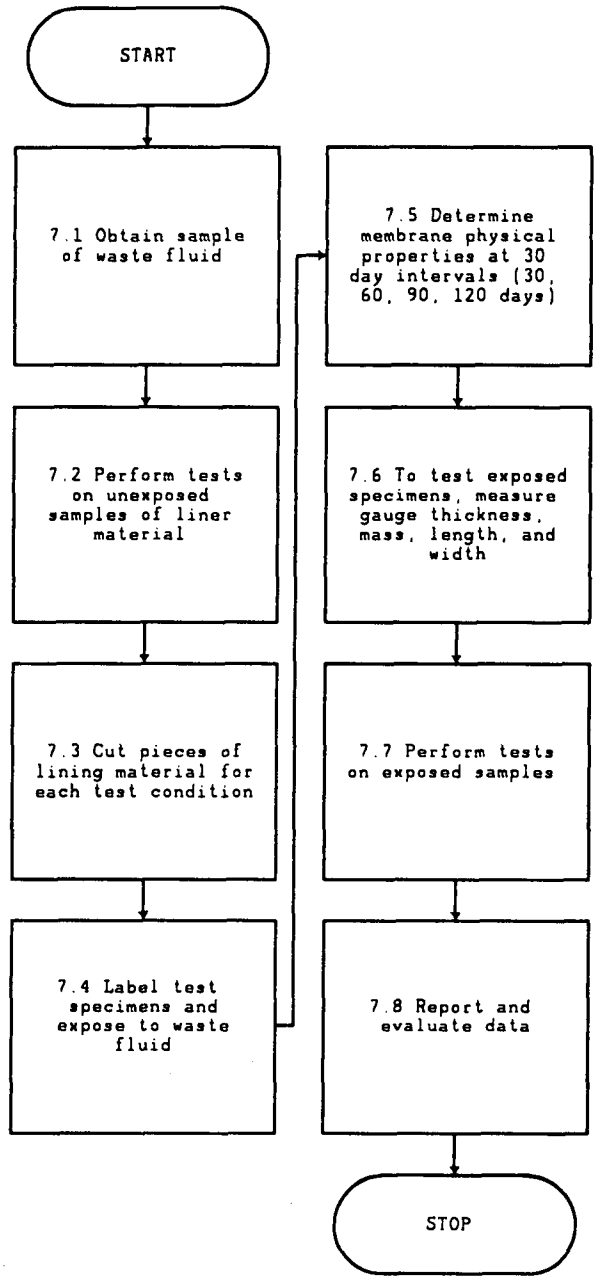


FIGURE 4. DIE FOR TENSILE DUMBBELL (NONREINFORCED LINERS) HAVING THE FOLLOWING DIMENSIONS:



W	- Width of narrow section	0.25 inches
L	- Length of narrow section	1.25 inches
WO	- Width overall	0.625 inches
LO	- Length overall	3.50 inches
G	- Gage length	1.00 inches
D	- Distance between gaps	2.00 inches


START
7.1 Obtain sample of waste fluid
7.2 Perform tests on unexposed samples of liner material
7.3 Cut pieces of lining material for each test condition
7.4 Label test specimens and expose to waste fluid
7.5 Determine membrane physical properties at 30 day intervals (30, 60, 90, 120 days)
7.6 To test exposed specimens, measure gauge thickness, mass, length, and width
7.7 Perform tests on exposed samples
7.8 Report and evaluate data
STOP

METHOD 9095

PAINT FILTER LIQUIDS TEST

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the presence of free liquids in a representative sample of waste.

1.2 The method is used to determine compliance with 40 CFR 264.314 and 265.314.

2.0 SUMMARY OF METHOD

2.1 A predetermined amount of material is placed in a paint filter. If any portion of the material passes through and drops from the filter within the 5-min test period, the material is deemed to contain free liquids.

3.0 INTERFERENCES

3.1 Filter media were observed to separate from the filter cone on exposure to alkaline materials. This development causes no problem if the sample is not disturbed.

4.0 APPARATUS AND MATERIALS

4.1 Conical paint filter: Mesh number 60 (fine meshed size). Available at local paint stores such as Sherwin-Williams and Glidden for an approximate cost of $0.07 each.

4.2 Glass funnel: If the paint filter, with the waste, cannot sustain its weight on the ring stand, then a fluted glass funnel or glass funnel with a mouth large enough to allow at least 1 in. of the filter mesh to protrude should be used to support the filter. The funnel is to be fluted or have a large open mouth in order to support the paint filter yet not interfere with the movement, to the graduated cylinder, of the liquid that passes through the filter mesh.

4.3 Ring stand and ring, or tripod.

4.4 Graduated cylinder or beaker: 100-mL.

5.0 REAGENTS

5.1 None.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected according to the directions in Chapter Nine of this manual.

6.2 A 100-mL or 100-g representative sample is required for the test. If it is not possible to obtain a sample of 100 mL or 100 g that is sufficiently representative of the waste, the analyst may use larger size samples in multiples of 100 mL or 100 g, i.e., 200, 300, 400 mL or g. However, when larger samples are used, analysts shall divide the sample into 100-mL or 100-g portions and test each portion separately. If any portion contains free liquids, the entire sample is considered to have free liquids.

7.0 PROCEDURE

7.1 Assemble test apparatus as shown in Figure 1.

7.2 Place sample in the filter. A funnel may be used to provide support for the paint filter.

7.3 Allow sample to drain for 5 min into the graduated cylinder.

7.4 If any portion of the test material collects in the graduated cylinder in the 5-min period, then the material is deemed to contain free liquids for purposes of 40 CFR 264.314 and 265.314.

8.0 QUALITY CONTROL

8.1 Duplicate samples should be analyzed on a routine basis.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

10.1 None required.

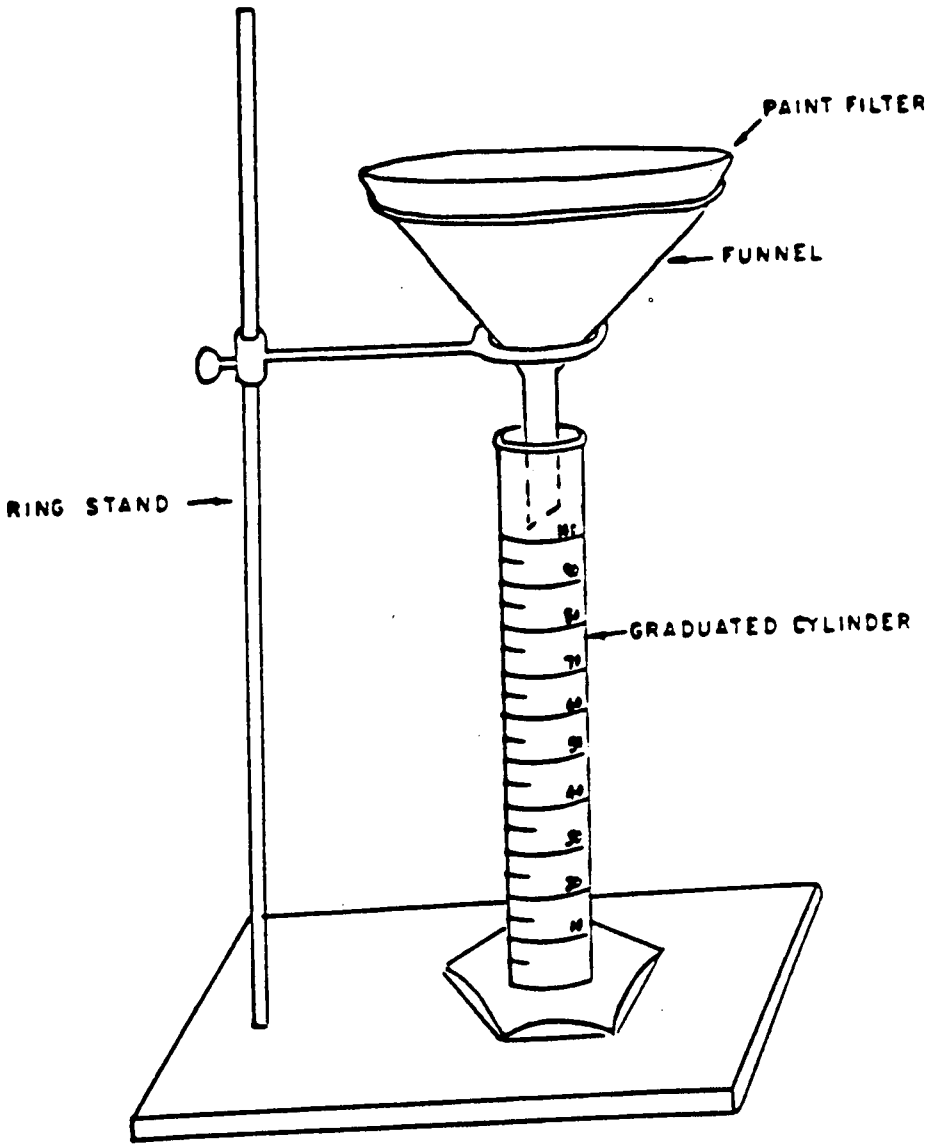
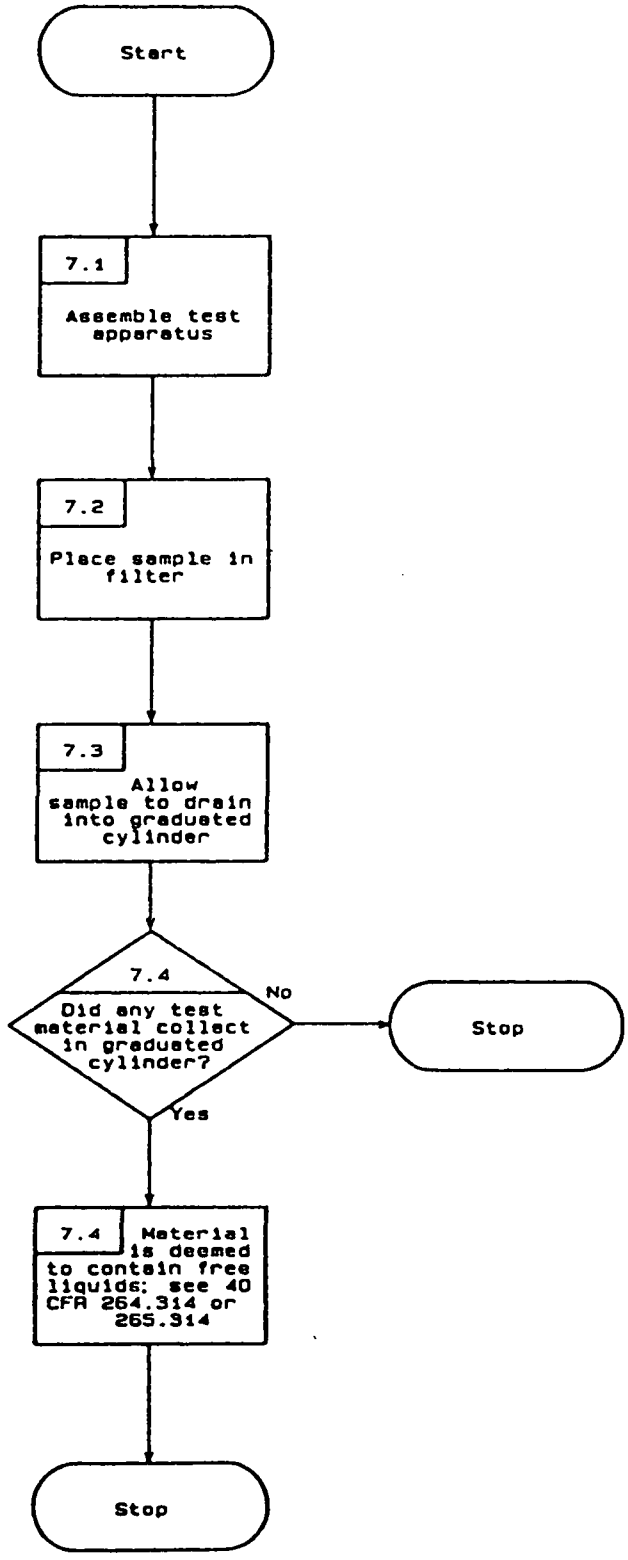


Figure 1. Paint filter test apparatus.


Start
7.1
Assemble test apparatus
7.2
Place sample in filter
7.3
Allow sample to drain into graduated cylinder
7.4
Did any test material collect in graduated cylinder?
No
Stop
Yes
7.4
Material is deemed to contain free liquids; see 40 CFR 264.314 or 265.314
Stop

METHOD 9096

LIQUID RELEASE TEST (LRT) PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 The Liquid Release Test (LRT) is a laboratory test designed to determine whether or not liquids will be released from sorbents when they are subjected to overburden pressures in a landfill.

1.2 Any liquid-loaded sorbent that fails the EPA Paint Filter Free Liquids Test (PFT) (SW-846 Method 9095), may be assumed to release liquids in this test. Analysts should ensure that the material in question will pass the PFT before performing the LRT.

2.0 SUMMARY OF METHOD

2.1 A representative sample of the liquid-loaded sorbent, standing 10 cm high in the device, is placed between twin stainless steel screens and two stainless-steel grids, in a device capable of simulating landfill overburden pressures. An absorptive filter paper is placed on the side of each stainless-steel grid opposite the sample (i.e., the stainless-steel screen separates the sample and the filter paper, while the stainless-steel grid provides a small air gap to prevent wicking of liquid from the sample onto the filter paper). A compressive force of 50 psi is applied to the top of the sample. Release of liquid is indicated when a visible wet spot is observed on either filter paper.

3.0 INTERFERENCES

3.1 When testing sorbents are loaded with volatile liquids (e.g., solvents), any released liquid migrating to the filter paper may rapidly evaporate. For this reason, filter papers should be examined immediately after the test has been conducted.

3.2 It is necessary to thoroughly clean and dry the stainless-steel screens prior to testing to prevent false positive or false negative results. Material caught in screen holes may impede liquid transmission through the screen causing false negative results. A stiff bristled brush, like those used to clean testing sieves, may be used to dislodge material from holes in the screens. The screens should be ultrasonically cleaned with a laboratory detergent, rinsed with deionized water, rinsed with acetone, and thoroughly dried.

When sorbents containing oily substances are tested, it may be necessary to use solvents (e.g., methanol or methylene chloride) to remove any oily residue from the screens and from the sample holder surfaces.

3.3 When placing the 76 mm screen on top of the loaded sample it is important to ensure that no sorbent is present on top of the screen to contact the filter paper and cause false positive results. In addition, some sorbent residue may adhere to container sidewalls and contact the filter as the sample

compresses under load, causing wet spots on the edges of the filter. This type of false positive may be avoided by carefully centering the 76 mm filter paper in the device prior to initiating the test.

3.4 Visual examination of the sample may indicate that a release is certain (e.g., free standing liquid or a sample that flows like a liquid), raising concern over unnecessary clean-up of the LRT device. An optional 5 minute Pre-Test, described in Appendix A of this procedure, may be used to determine whether or not an LRT must be performed.

4.0 APPARATUS AND MATERIALS

4.1 LRT Device (LRTD): A device capable of applying 50 psi of pressure continuously to the top of a confined, cylindrical sample (see Figure 1). The pressure is applied by a piston on the top of the sample. All device components contacting the sample (i.e., sample-holder, screens, and piston) should be resistant to attack by substances being tested. The LRTD consists of two basic components, described below.

4.1.1 Sample holder: A rigid-wall cylinder, with a bottom plate, capable of holding a 10 cm high by 76 mm diameter sample.

4.1.2 Pressure Application Device: In the LRTD (Figure 1), pressure is applied to the sample by a pressure rod pushing against a piston that lies directly over the sample. The rod may be pushed against the piston at a set pressure using pneumatic, mechanical, or hydraulic pressure. Pneumatic pressure application devices should be equipped with a pressure gauge accurate to within $\pm$ 1 psi, to indicate when the desired pressure has been attained and whether or not it is adequately maintained during the test. Other types of pressure application devices (e.g., mechanical or hydraulic) may be used if they can apply the specified pressure continuously over the ten minute testing time. The pressure application device must be calibrated by the manufacturer, using a load cell or similar device placed under the piston, to ensure that 50 $\pm$ 1 psi is applied to the top of the sample. The pressure application device should be sufficiently rugged to deliver consistent pressure to the sample with repeated use.

4.2 Stainless-Steel Screens: To separate the sample from the filter, thereby preventing false positive results from particles falling on the filter paper. The screens are made of stainless steel and have hole diameters of 0.012 inches with 2025 holes per square inch. Two diameters of screens are used: a larger (90 mm) screen beneath the sample and a smaller (76 mm) screen that is placed on top of the sample in the sample-holding cylinder.

4.3 Stainless-Steel Grids: To provide an air gap between the stainless-steel screen and filter paper, preventing false positive results from capillary action. The grids are made of 1/32" diameter, woven, stainless steel wire cut to two diameters, 90 mm and 76 mm.

4.4 Filter Papers: To detect released liquid. Two sizes, one 90 mm and one 76 mm, are placed on the side of the screen opposite the sample. The 76 mm diameter filter paper has the outer 6 mm cut away except 3 conical points used for centering the paper (see Figure 2). Blue, seed-germination filter paper manufactured by Schleicher and Schuell (Catalog Number 33900) is suitable. Other colored, absorptive papers may be used as long as they provide sufficient wet/dry contrast for the operator to clearly see a wet spot.

4.5 Spatula: To assist in loading and removing the sample.

4.6 Rubber or wooden mallet: To tap the sides of the device to settle and level the sample.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Acetone.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 All samples should be collected using a sampling plan that addresses the considerations discussed in "Test Methods for Evaluating Solid Wastes (SW-846)." The sampling plan should be designed to detect and sample any pockets of liquids that may be present in a container (i.e., in the bottom or top of the container).

6.2 Preservatives should not be added to samples.

6.3 Samples should be tested as soon as possible after collection, but in no case after more than three days after collection. If samples must be stored, they can be stored in sealed containers and maintained under dark, cool conditions (temperature ranging between 35° and 72° F). Samples should not be frozen.

7.0 PROCEDURE

The procedure below was developed for the original LRTD, manufactured by Associated Design and Manufacturing Company (ADM). Procedures for other LRTDs, along with evidence for equivalency to the ADM device, should be supplied by the manufacturer.

7.1 Disassemble the LRTD and make sure that all parts are clean and dry.

7.2 Invert the sample-holding cylinder and place the large stainless-steel screen, the large stainless-steel grid, then a 90 mm filter paper on the cylinder base (bottom-plate side).

7.3 Secure the bottom plate (plate with a hole in the center and four holes located on the outer circumference) to the flange on the bottom of the sample-holding cylinder using four knob screws.

7.4 Turn the sample holder assembly to the right-side-up position (bottom-plate-side down). Fill the sample holder with a representative sample until the sample height measures 10 cm (up to the etched line in the cylinder).

7.5 Tap the sides of the sample holder with a rubber or wooden mallet to remove air pockets and to settle and level the sample.

7.6 Repeat filling, and tapping until a sample height of 10 cm is maintained after tapping.

7.7 Smooth the top of the sample with a spatula to create a horizontal surface.

7.8 Place the small stainless-steel screen, then the small stainless-steel grid on top of the sample.

> NOTE: Prior to placing the stainless-steel grid on top of the screen, make sure that no sorbent material is on the grid side of the stainless-steel screen.

7.9 Place the 76 mm filter paper on top of the small stainless-steel grid, making sure the filter paper is centered in the device.

7.10 Using the piston handle (screwed into the top of the piston) lower the piston into the sample holder until it sits on top of the filter paper. Unscrew and remove the handle.

7.11 Place the loaded sample holder into position on the baseplate and lock into place with two toggle clamps.

7.12 Place the pressure application device on top of the sample-holder. Rotate the device to lock it into place and insert the safety key.

7.13 Connect air lines.

7.14 Initiate rod movement and pressure application by pulling the air-valve lever toward the operator and note time on data sheet. The pressure gauge at the top of the pressure application device should read as specified in the factory calibration record for the particular device. If not, adjust regulator to attain the specified pressure.

NOTE: After pressure application, the air lines can be disconnected, the toggle clamps can be released, and the LRTD can be set aside for 10 minutes while other LRTDs are pressurized. LRTD pressures should be checked every 3 minutes to ensure that the specified pressure is being maintained. If the specified pressure is not being maintained to within ± 5 psi, the LRTD must be reconnected to the air lines and pressure applied throughout the 10 minute test.

7.15 After 10 minutes place the LRTD on the baseplate, reconnect air lines and toggle clamps, and turn off pressure (retract the rod) by pushing the air-valve lever away from the operator. Note time on data sheet.

7.16 When the air gauge reaches 0 psi, disconnect the air lines and remove the pressure-application device by removing the safety key, rotating the device, and lifting it away from the sample holder.

7.17 Screw the piston handle into the top of the piston.

7.18 Lift out the piston.

7.19 Remove the filter paper and immediately examine it for wet spots (wet area on the filter paper). The presence of a wet spot(s) indicates a positive test (i.e., liquid release). Note results on data sheet.

7.20 Release toggle clamps and remove sample holder from baseplate. Invert sample holder onto suitable surface and remove the knob screws holding the bottom plate.

7.21 Remove the bottom plate and immediately examine the filter paper for wet spots as described in Step 7.19. Note results on data sheet. Wet spot(s) on either filter indicates a positive test.

8.0 QUALITY CONTROL

8.1 Duplicate samples should be analyzed every twenty samples or every analytical batch, whichever is more frequent. Refer to Chapter One for additional QC protocols.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are not available at this time.

10.0 REFERENCES

1. Hoffman, P., G. Kingsbury, B. Lesnik, M. Meyers, "Background Document for the Liquid Release Test (LRT) Procedure"; document submitted to the Environmental Protection Agency by Research Triangle Institute: Research Triangle Park, NC under Contract No. 68-01-7075, Work Assignment 76 and Contract No. 68-WO-0032, Work Assignment 12.

FIGURE 1.
LRT DEVICE

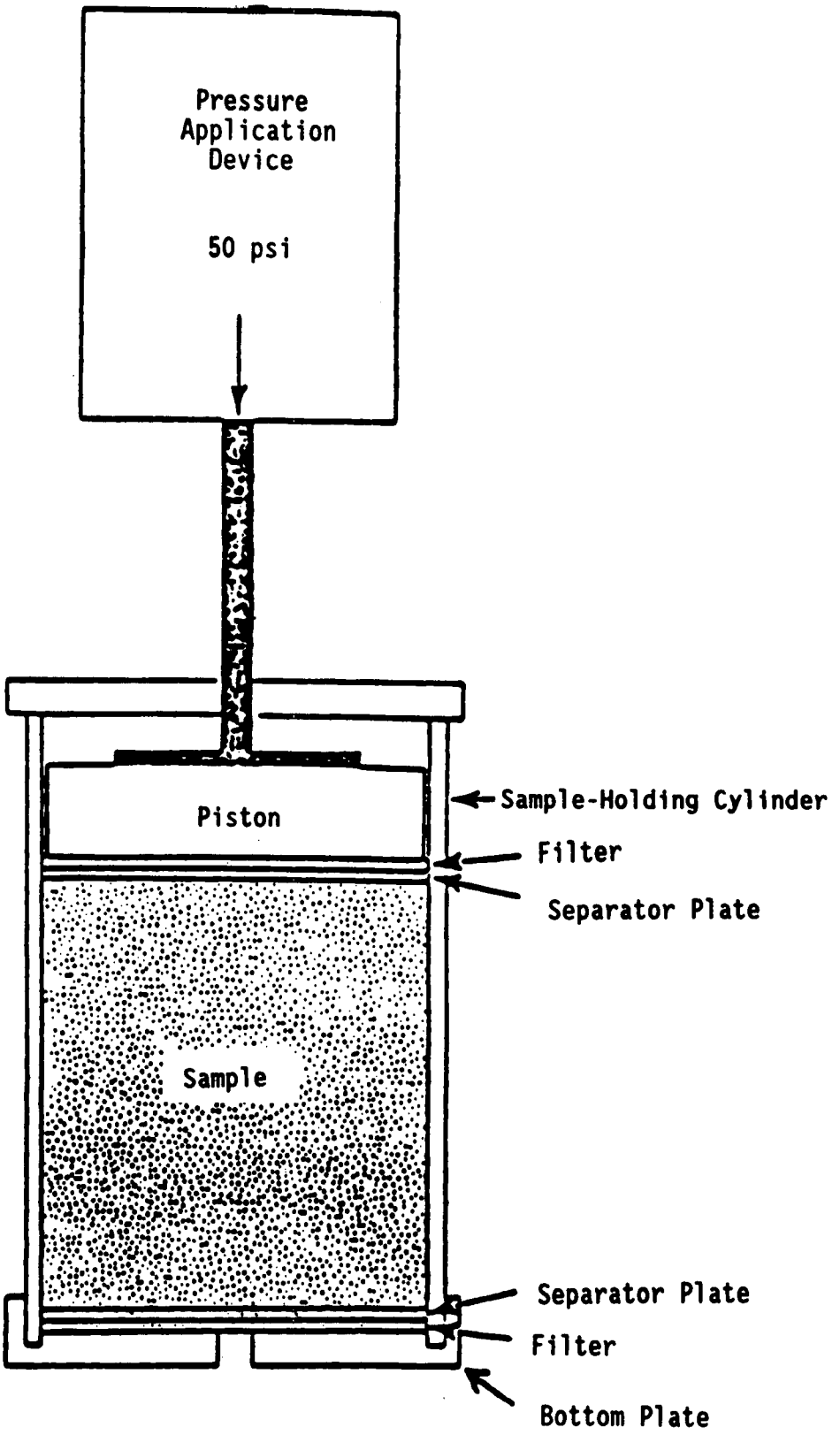


FIGURE 2.
76 MM DIAMETER FILTER PAPER

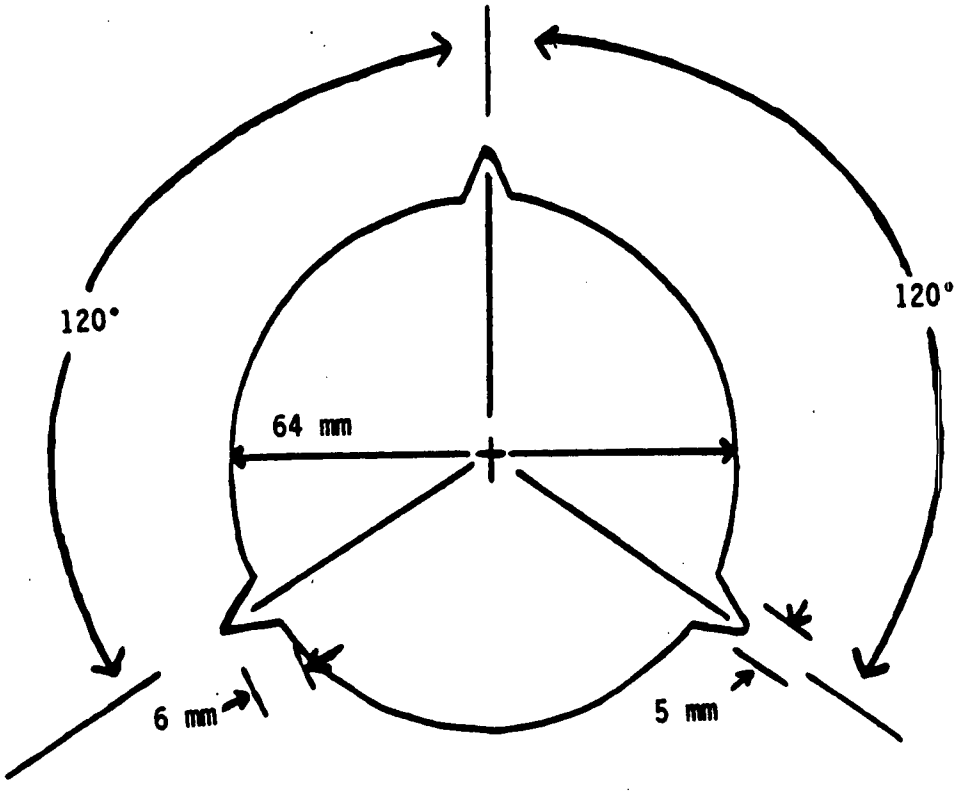


FIGURE 3.
GLASS GRID SPECIFICATIONS.

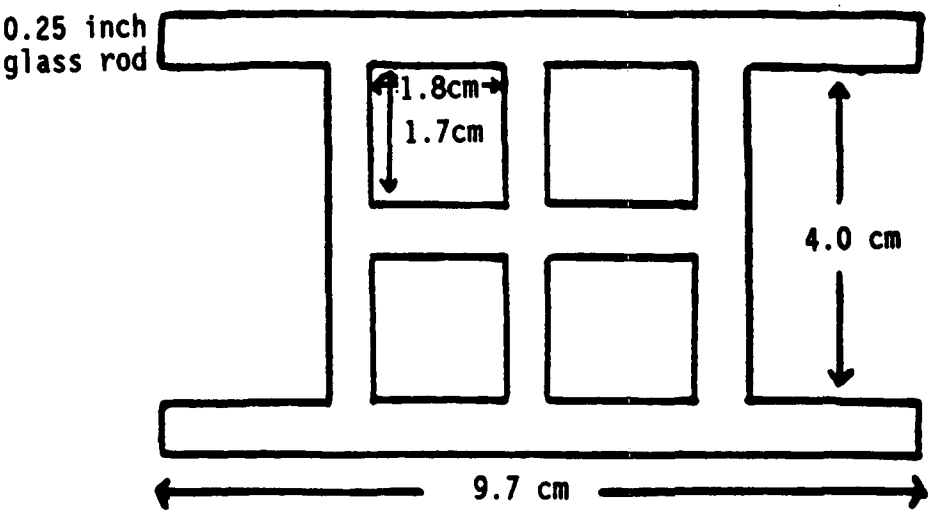
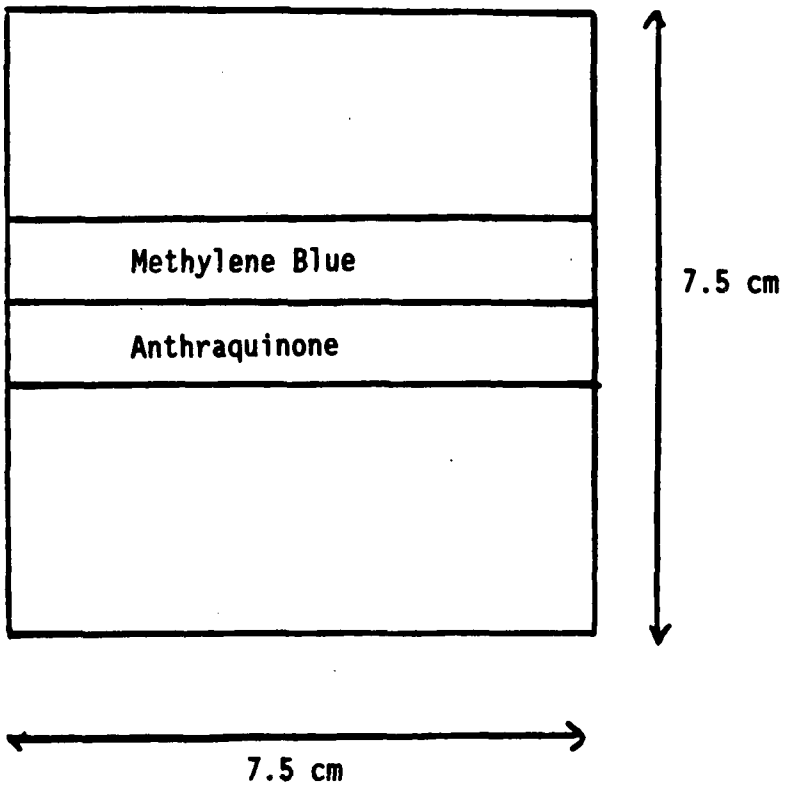
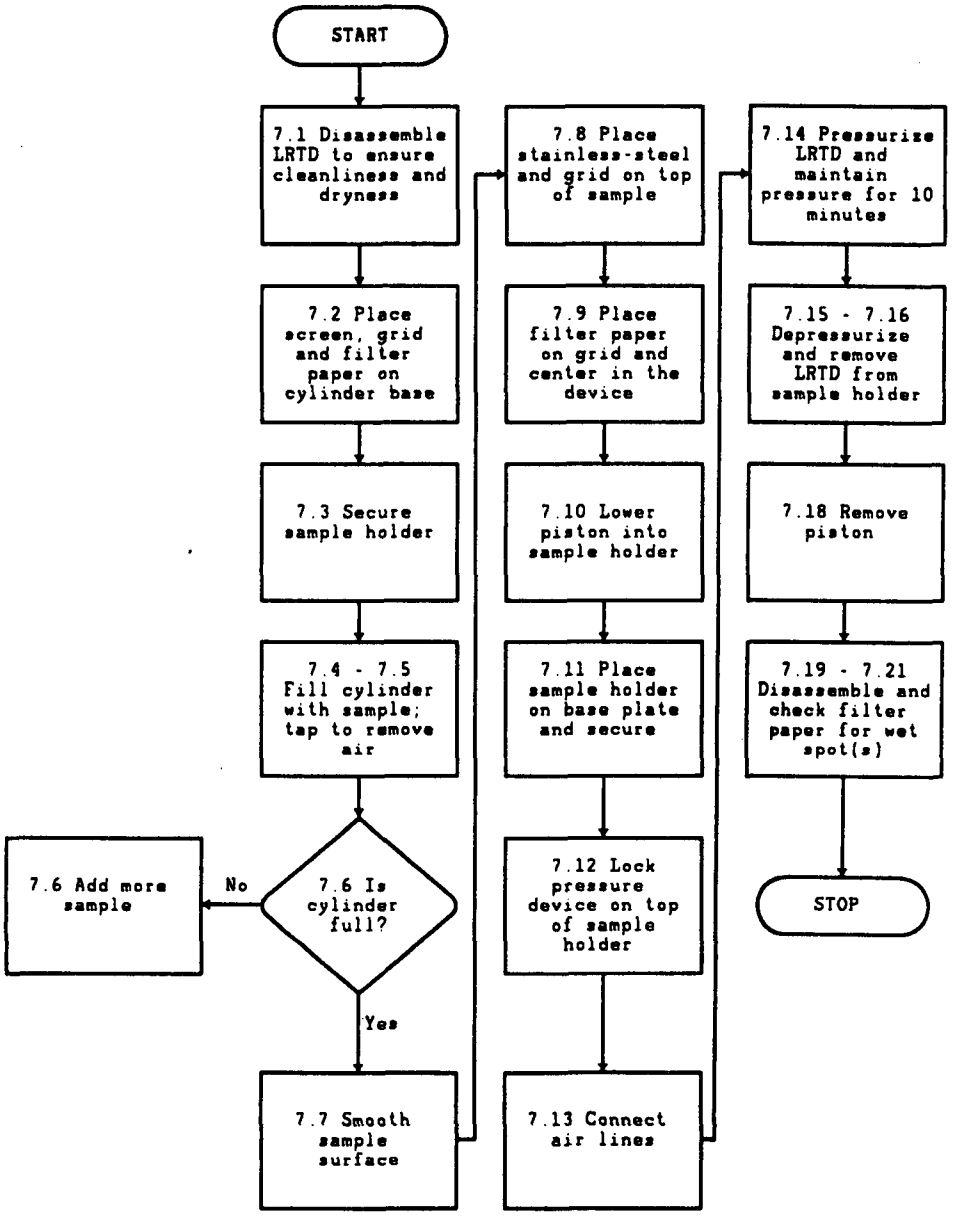


FIGURE 4.
POSITIONING OF DYE ON GLASS PLATE




START
7.1 Disassemble LRTD to ensure cleanliness and dryness
7.2 Place screen, grid and filter paper on cylinder base
7.3 Secure sample holder
7.4 - 7.5 Fill cylinder with sample; tap to remove air
7.6 Is cylinder full?
No
7.6 Add more sample
Yes
7.7 Smooth sample surface
7.8 Place stainless-steel and grid on top of sample
7.9 Place filter paper on grid and center in the device
7.10 Lower piston into sample holder
7.11 Place sample holder on base plate and secure
7.12 Lock pressure device on top of sample holder
7.13 Connect air lines
7.14 Pressurize LRTD and maintain pressure for 10 minutes
7.15 - 7.16 Depressurize and remove LRTD from sample holder
7.18 Remove piston
7.19 - 7.21 Disassemble and check filter paper for wet spot(s)
STOP

APPENDIX A

LIQUID RELEASE TEST PRE-TEST

1.0 SCOPE AND APPLICATION

1.1 The LRT Pre-Test is an optional, 5 minute laboratory test designed to determine whether or not liquids will be definitely released from sorbents before applying the LRT. This test is performed to prevent unnecessary cleanup and possible damage to the LRT device.

1.2 This test is purely optional and completely up to the discretion of the operator as to when it should be used.

2.0 SUMMARY OF METHOD

A representative sample will be loaded into a glass grid that is placed on a glass plate already stained with 2 dyes (one water soluble and one oil soluble). A second glass plate will be placed on top and a 2 lb. weight placed on top for 5 minutes. At the end of 5 minutes the base of the glass grid is examined for any dye running along the edges, this would indicate a liquid release.

3.0 INTERFERENCES

A liquid release can be detected at lower Liquid Loading Levels with extremely clean glassware. The glass plates and glass grid should be cleaned with a laboratory detergent, rinsed with Deionized water, rinsed with acetone, and thoroughly dried.

4.0 APPARATUS AND MATERIALS

4.1 Glass Plate: 2 glass plates measuring 7.5 cm x 7.5 cm.

4.2 Glass Grid: See Figure 3.

4.3 Paint Brush: Two small paint brushes for applying dyes.

4.4 Spatula: To assist in loading the sample.

4.5 Weight: 2.7 kg weight to apply pressure to the sample.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Methylene Blue dye in methanol.

5.3 Anthraquinone dye in toluene.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

See LRT Procedure.

7.0 PROCEDURE

7.1 Paint one strip, approximately 1 cm wide, of methylene blue dye across the center of a clean and dry glass plate (see Figure 4). The dye is allowed to dry.

7.2 Paint one strip, approximately 1 cm wide, of anthraquinone dye across the center of the same glass plate (see Figure 4). This strip should be adjacent to and parallel with the methylene blue strip. The dye is allowed to dry.

7.3 Place the glass grid in the center of the dye-painted glass plate.

7.4 Place a small amount of sample into the glass-grid holes, pressing down gently until the holes are filled to slightly above the grid top.

7.5 Place a second, clean and dry, glass plate on top of the sample and grid.

7.6 Place a 2.7 kg weight on top of the glass for 5 minutes.

7.7 After 5 minutes remove the weight and examine the base of the grid extending beyond the sample holes for any indication of dyed liquid. The entire assembly may be turned upside down for observation. Any indication of liquid constitutes a release and the LRT does not need to be performed.

8.0 QUALITY CONTROL

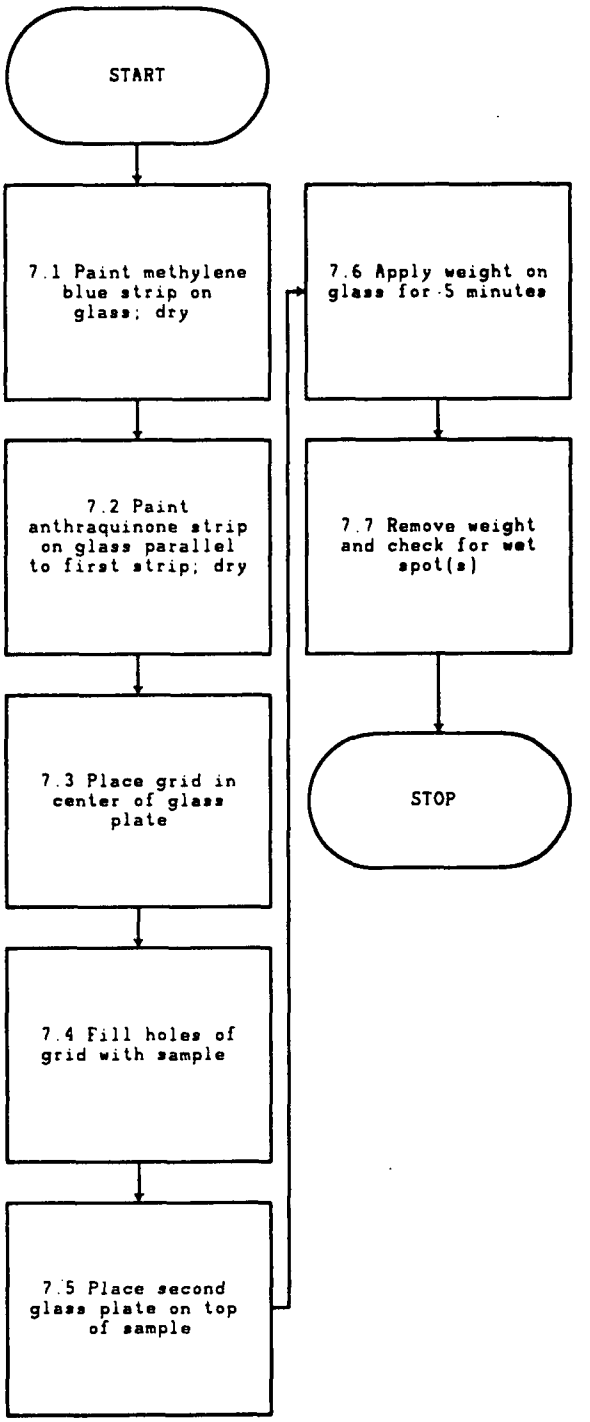
8.1 Refer to Chapter One for specific quality control procedures.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are not available at this time.

10.0 REFERENCES

1. Research Triangle Institute. "Background Document for the Liquid Release Test: Single Laboratory Evaluation and 1988 Collaborative Study". Submitted to the Environmental Protection Agency under Contract No. 68-01-7075, Work Assignment 76 and Contract No. 68-WO-0032, Work Assignment 12. September 18, 1991.


START
7.1 Paint methylene blue strip on glass; dry
7.2 Paint anthraquinone strip on glass parallel to first strip; dry
7.3 Place grid in center of glass plate
7.4 Fill holes of grid with sample
7.5 Place second glass plate on top of sample
7.6 Apply weight on glass for 5 minutes
7.7 Remove weight and check for wet spot(s)
STOP

METHOD 9100

SATURATED HYDRAULIC CONDUCTIVITY, SATURATED LEACHATE CONDUCTIVITY, AND INTRINSIC PERMEABILITY

1.0 INTRODUCTION

1.1 Scope and Application: This section presents methods available to hydrogeologists and and geotechnical engineers for determining the saturated hydraulic conductivity of earth materials and conductivity of soil liners to leachate, as outlined by the Part 264 permitting rules for hazardous-waste disposal facilities. In addition, a general technique to determine intrinsic permeability is provided. A cross reference between the applicable part of the RCRA Guidance Documents and associated Part 264 Standards and these test methods is provided by Table A.

1.1.1 Part 264 Subpart F establishes standards for ground water quality monitoring and environmental performance. To demonstrate compliance with these standards, a permit applicant must have knowledge of certain aspects of the hydrogeology at the disposal facility, such as hydraulic conductivity, in order to determine the compliance point and monitoring well locations and in order to develop remedial action plans when necessary.

1.1.2 In this report, the laboratory and field methods that are considered the most appropriate to meeting the requirements of Part 264 are given in sufficient detail to provide an experienced hydrogeologist or geotechnical engineer with the methodology required to conduct the tests. Additional laboratory and field methods that may be applicable under certain conditions are included by providing references to standard texts and scientific journals.

1.1.3 Included in this report are descriptions of field methods considered appropriate for estimating saturated hydraulic conductivity by single well or borehole tests. The determination of hydraulic conductivity by pumping or injection tests is not included because the latter are considered appropriate for well field design purposes but may not be appropriate for economically evaluating hydraulic conductivity for the purposes set forth in Part 264 Subpart F.

1.1.4 EPA is not including methods for determining unsaturated hydraulic conductivity at this time because the Part 264 permitting standards do not require such determinations.

1.2 Definitions: This section provides definitions of terms used in the remainder of this report. These definitions are taken from U.S. Government publications when possible.

TABLE A

HYDRAULIC AND LINER CONDUCTIVITY DETERMINATION METHODS FOR SURFACE IMPOUNDMENT, WASTE PILE, AND LANDFILL COMPONENTS, AS CITED IN RCRA GUIDANCE DOCUMENTS AND DESCRIBED IN SW-846

Surface Impoundments	Guidance Cite[1] Associated Regulation	Corresponding SW-846 Section
Soil liner hydraulic conductivity	Guidance section D(2)(b)(1) and D(2)(c)(1)/Section 264.221(a),(b)	2.0
Soil liner leachate conductivity	Guidance section D(2)(b)(2) and D(2)(c)(2)	2.11
Leak detection	Guidance section C(2)(a)/ Section 264.222	2.0
Final cover drain layer	Guidance section E(2)(d)(1) Section 264.228	2.0
Final cover low permeability layer	Guidance section E(2)(e)(2)(A)/ Section 264.228	2.0
General hydrogeologic site investigation	264 subpart F	3.0

[1] RCRA Guidance Document: Surface Impoundments, Liner Systems, Final Cover, and Freeboard Control. Issued July, 1982.

(continued on next page)

TABLE A (continued)

Waste Piles	Guidance Cite[2] Associated Regulation	Corresponding SW-846 Section
Soil liner hydraulic conductivity	Guidance section D(2)(b)(i) and D(2)(c)(i)/ Section 264.251(a)(1)	2.0
Soil liner leachate conductivity	Guidance section D(2)(b)(ii) and D(2)(c)(ii)	2.11
Leak detection system	Guidance section C(2)(a)/ Section 264.252(a)	2.0
Leachate collection and renewal system	Guidance section C(2)(a)/ Section 264.251(a)(2)	2.0
General hydrogeologic site investigation	264 subpart F	3.0

[2] RCRA Guidance Document: Waste Pile Design, Liner Systems. Issued July, 1982.

(continued on next page)

TABLE A (continued)

Landfills	Guidance Cite[3] Associated Regulation	Corresponding SW-846 Section
Soil liner hydraulic conductivity	Guidance section D(2)(b)(1)/ Section 264.301(a)(1)	2.0
Soil liner leachate conductivity	Guidance section D(2)(b)(2)	2.11
Leak detection system	Guidance section C(2)(a)/ Section 264.302(a)(3)	2.0
Leachate collection and removal system	Guidance section C(2)(a)/ Section 264.301(a)(2)	2.0
Final cover drain layer	Guidance section E(2)(d)(1)/ Section 264.310(a)(b)	2.0
Final cover low permeability layer	Guidance section E(2)(e)(2)(A) Section 264.310(a)(b)	2.0
General hydrogeologic site investigation	264 subpart F	3.0

[3] RCRA Guidance Document: Landfill Design, Liner Systems and Final Cover. Issued July, 1982.

1.2.1 **Units:** This report uses consistent units in all equations. The symbols used are:

Length = L,
Mass = M, and
Time = T.

1.2.2 **Fluid potential or head** (h): A measure of the potential energy required to move fluid from a point in the porous medium to a reference point. For virtually all situations expected to be found in disposal sites and in ground water systems, h is defined by the following equation:

$$h = h_p + h_z \quad (1)$$

where:

h is the total fluid potential, expressed as a height of fluid above a reference datum, L;

h_p, the pressure potential caused by the weight of fluid above the point in question, L, is defined by $h_p = P/\rho g$,

where:

P is the fluid pressure at the point in question, $ML^{-1}T^{-2}$,

ρ is the fluid density at the prevailing temperature, ML^{-3}, and

g is the acceleration of gravity, LT^{-2}; and

h_z is the height of the point in question above the reference datum, L.

By knowing h_p and h_z at two points along a flow path and by knowing the distance between these points, the fluid potential gradient can be determined.

1.2.3 **Hydraulic potential or head:** The fluid potential when water is the fluid.

1.2.4 **Hydraulic conductivity:** The fluid potential when water is the fluid. The generic term, fluid conductivity, is discussed below in 1.2.5.

1.2.5 **Fluid conductivity** (K): Defined as the volume of fluid at the prevailing density and dynamic viscosity that will move in a unit time under a unit fluid potential gradient through a unit area measured at right angles to the direction of flow. It is a property of both the fluid and the porous medium as shown by the following equation:

$$K = \frac{k\rho g}{u} \; ; \qquad (2)$$

where:

K is the fluid conductivity, LT^{-1};

k is the intrinsic permeability, a property of the porous medium alone, L^2; and

u is the dynamic viscosity of the fluid at the prevailing temperature, $ML^{-1}\ T^{-1}$.

The fluid conductivity of a porous material is also defined by Darcy's law, which states that the fluid flux (q) through a porous medium is proportional to the first power of the fluid potential across the unit area:

$$q = \frac{Q}{A} = -KI \qquad (3)$$

where:

q = the specific fluid flux, LT^{-1},

Q is the volumetric fluid flux, L^3T^{-1},

A is the cross-sectional area, L^2, and

I is the fluid potential gradient, L^0.

Darcy's law provides the basis for all methods used to determine hydraulic conductivity in this report. The range of validity of Darcy's law is discussed in Section 1.5 (Lohman, 1972).

1.2.6 **Leachate conductivity:** The fluid conductivity when leachate is the fluid.

1.2.7 **Aquifer:** A geologic formation, group of formations, or part of a formation capable of yielding a significant amount of ground water to wells or springs (40 CFR 260.10).

1.2.8 **Confining layer:** By strict definition, a body of impermeable material stratigraphically adjacent to one or more aquifers. In nature, however, its hydraulic conductivity may range from nearly zero to some value distinctly lower than that of the aquifer. Its conductivity relative to that of the aquifer it confines should be specified or indicated by a suitable modifier, such as "slightly permeable" or "moderately permeable" (Lohman, 1972).

1.2.9 **Transmissivity, T [L^2, T^{-1}]:** The rate at which water of the prevailing kinematic viscosity is transmitted through a unit width of the aquifer under a unit hydraulic gradient. Although spoken of as a

property of the aquifer, the term also includes the saturated thickness of the aquifer and the properties of the fluid. It is equal to an integration of the hydraulic conductivities across the saturated part of the aquifer perpendicular to the flow paths (Lohman, 1972).

1.3 Temperature and viscosity corrections: By using Equation (2), corrections to conditions different from those prevailing during the test can be made. Two types of corrections can commonly be made: a correction for a temperature that varies from the test temperature, and a correction for fluids other than that used for the test. The temperature correction is defined by:

$$K_f = \frac{K_t \, u_t \, \rho_f}{u_f \, \rho_t} \tag{4}$$

where:

the subscript f refers to field conditions, and

the subscript t refers to test conditions.

Most temperature corrections are necessary because of the dependence of viscosity on temperature. Fluid density variations caused by temperature changes are usually very small for most liquids. The temperature correction for water can be significant. Equation (4) can also be used to determine hydraulic conductivity if fluids other than water are used. It is assumed, however, when using Equation (4) that the fluids used do not alter the intrinsic permeability of the porous medium during the test. Experimental evidence shows that this alteration does occur with a wide range of organic solvents (Anderson and Brown, 1981). Consequently, it is recommended that tests be run using fluids, such as leachates, that might occur at each particular site. Special considerations for using non-aqueous fluids are given in Section 3.3 of this report.

1.4 Intrinsic permeability (k): Rearrangement of Equation 2 results in a definition of intrinsic permeability:

$$k = \frac{Ku}{\rho g} \, . \tag{5}$$

Since this is a property of the medium alone, if fluid properties change, the fluid conductivity must also change to keep the intrinsic permeability a constant. By using measured fluid conductivity, and values of viscosity and density for the fluid at the test temperature, intrinsic permeability can be determined.

1.5 Range of validity of Darcy's law: Determination of fluid conductivities using both laboratory and field methods requires assuming the validity of Darcy's law. Experimental evidence has shown that deviations from the linear dependence of fluid flux on potential gradient exist for both extremely low and extremely high gradients (Hillel, 1971; Freeze and Cherry, 1979). The lower limits are the result of the existence of threshold

gradients required to initiate flow (Swartzendruber, 1962). The upper limits to the validity of Darcy's law can be estimated by the requirements that the Reynolds number, Re, in most cases be kept below 10 (Bear, 1972). The Reynolds number is defined by:

$$Re = \frac{\rho q d}{u} \tag{6}$$

where:

d is some characteristic dimension of the system, often represented by the median grain size diameter, D_{50}, (Bouwer, 1978), and

q is the fluid flux per unit area, LT^{-1}.

For most field situations, the Reynolds number is less than one, and Darcy's law is valid. However, for laboratory tests it may be possible to exceed the range of validity by the imposition of high potential gradients. A rough check on acceptable gradients can be made by substituting Darcy's law in Equation (6) and using an upper limit of 10 for Re:

$$I \leq \frac{10u}{\rho K D_{50}} \tag{7}$$

where:

K is the approximate value of fluid conductivity determined at gradient I.

A more correct check on the validity of Darcy's law or the range of gradients used to determine fluid conductivity is performed by measuring the conductivity at three different gradients. If a plot of fluid flux versus gradient is linear, Darcy's law can be considered to be valid for the test conditions.

1.6 Method Classification: This report classifies methods of determining fluid conductivity into two divisions: laboratory and field methods. Ideally, and whenever possible, compliance with Part 264 disposal facility requirements should be evaluated by using field methods that test the materials under in-situ conditions. Field methods can usually provide more representative values than laboratory methods because they test a larger volume of material, thus integrating the effects of macrostructure and heterogeneities. However, field methods presently available to determine the conductivity of compacted fine-grained materials in reasonable times require the tested interval to be below a water table or to be fairly thick, or require excavation of the material to be tested at some point in the test. The integrity of liners and covers should not be compromised by the installation of boreholes or piezometers required for the tests. These restrictions generally lead to the requirement that the fluid conductivity of liner and cover materials must be determined in the laboratory. The transfer value of laboratory data to field conditions can be maximized for liners and covers because it is possible to reconstruct relatively accurately the desired

field conditions in the laboratory. However, field conditions that would alter the values determined in the laboratory need to be addressed in permit applications. These conditions include those that would increase conductivity by the formation of microcracks and channels by repeated wetting and drying, and by the penetration of roots.

1.6.1 **Laboratory methods** are categorized in Section 2.0 by the methods used to apply the fluid potential gradient across the sample. The discussion of the theory, measurement, and computations for tests run under constant and falling-head conditions is followed by a detailed discussion of tests using specific types of laboratory apparatus and the applicability of these tests to remolded compacted, fine-grained uncompacted, and coarse-grained porous media. Section 2.3 provides a discussion of the special considerations for conducting laboratory tests using non-aqueous permeants. Section 2.10 gives a discussion of the sources of error and guidance for establishing the precision of laboratory tests. Laboratory methods may be necessary to measure vertical fluid conductivity. Values from field tests reflect effects of horizontal and vertical conductivity.

1.6.2 **Field methods** are discussed in Section 3.0 and are limited to those requiring a single bore hole or piezometer. Methods requiring multiple bore holes or piezometers and areal methods are included by reference. Because of the difficulties in determining fluid conductivity of in-place liner and cap materials under field conditions without damaging their integrity, the use of field methods for fine-grained materials will be generally restricted to naturally occurring materials that may serve as a barrier to fluid movement. Additional field methods are referenced that allow determination of saturated hydraulic conductivity of the unsaturated materials above the shallowest water table. General methods for fractured media are given in Section 3.8. A discussion of the important considerations in well installation, construction, and development is included as an introduction to Section 3.0.

2.0 LABORATORY METHODS

2.1 Sample collection for laboratory method: To assure that a reasonable assessment is made of field conditions at a disposal site, a site investigation plan should be developed to direct sampling and analysis. This plan generally requires$the professional judgement of an experienced hydrogeologist or geotechnical engineer. General guidance is provided for plan development in the Guidance Manual for Preparation of a Part 264 land Disposal Facility Permit Application (EPA, in press). The points listed below should be followed:

- The hydraulic conductivity of a soil liner should be determined either from samples that are processed to simulate the actual liner, or from an undisturbed sample of the complete liner.

- To obtain undisturbed samples, the thin-walled tube sampling method (ASTM Method # D1587-74) or a similar method may be used. Samples representative of each lift of the liner should be obtained, and used in the analyses. If actual undisturbed samples are not used, the soil used in liner construction must be processed to represent accurately the liner's initial water content and bulk density. The method described in Section 2.7.3 or ASTM Method #D698-70 (ASTM, 1978) can be used for this purpose.

- For purpose of the general site investigation, the general techniques presented in ASTM method #D420-69 (ASTM, 1978) should be followed. This reference establishes practices for soil and rock investigation and sampling, and incorporates various detailed ASTM procedures for investigation, sampling, and material classification.

2.2 Constant-head methods: The constant-head method is the simplest method of determining hydraulic conductivity of saturated soil samples. The concept of the constant-head method is schematically illustrated in Figure 1. The inflow of fluid is maintained at a constant head (h) above a datum and outflow (Q) is measured as a function of time (t). Using Darcy's law, the hydraulic conductivity can be determined using the following equation after the outflow rate has become constant:

$$K = QL/hA, \tag{8}$$

where:

K = hydraulic conductivity, LT^{-1};

L = length of sample, L;

A = cross-sectional area of sample, L^2;

Q = outflow rate, L^3T^{-1}; and

h = fluid head difference across the sample, L.

Constant-head methods should be restricted to tests on media having high fluid conductivity.

2.3 Falling-head methods: A schematic diagram of the apparatus for the falling-head method is shown in Figure 2. The head of inflow fluid decreases from h_1 to h_2 as a function of time (t) in a standpipe directly connected to the specimen. The fluid head at the outflow is maintained constant. The quantity of outflow can be measured as well as the quantity of inflow. For the setup shown in Figure 2a, the hydraulic conductivity can be determined using the following equation:

$$K = \frac{2.3\ aL}{At} \log_{10} \frac{h_0}{h_1}, \tag{9}$$

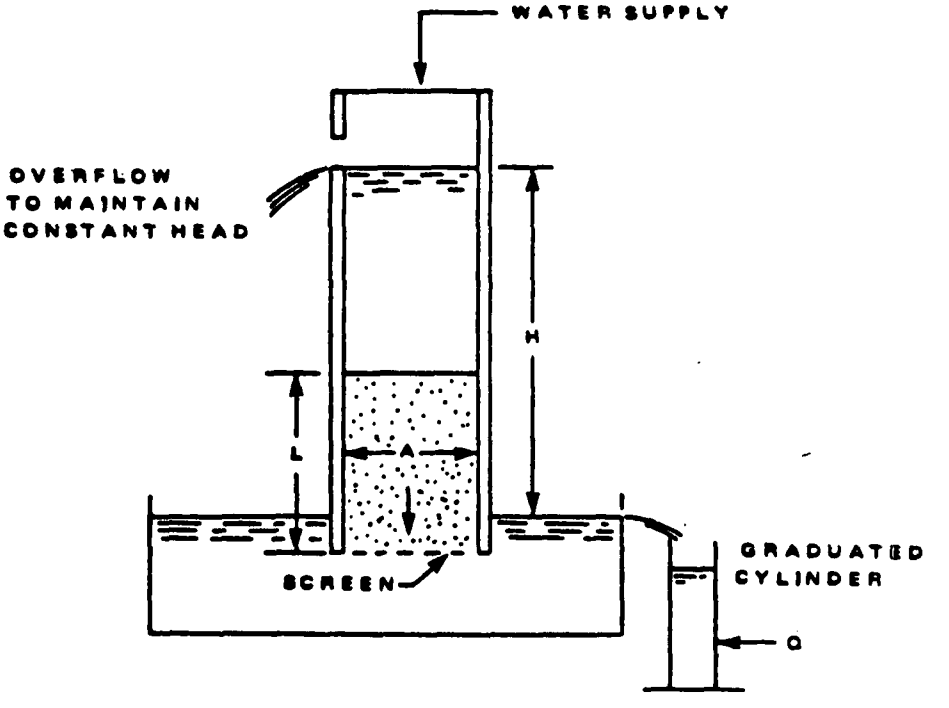


Figure 1.--Principle of the constant head method

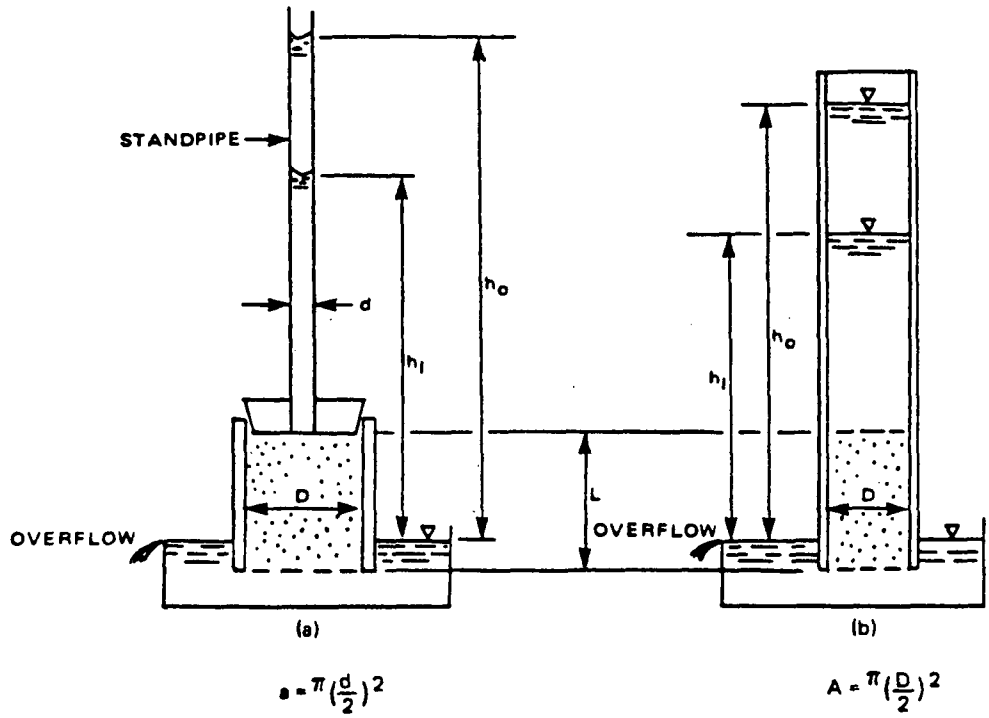


Figure 2.--Principle of the falling head method using a small (a) and large (b) standpipe.

where:

a = the cross-sectional area of the standpipe, L^2;

A = the cross-sectional area of the specimen, L^2;

L = the length of the specimen, L; and

t = elapsed time from t_1 to t_2, T.

For the setup in Figure 2b, the term a/A in Equation (9) is replaced by 1.0. Generally, falling-head methods are applicable to fine-grained soils because the testing time can be accelerated.

2.4 General test considerations:

2.4.1 **Fluid supplies to be used:** For determining hydraulic conductivity and leachate conductivity, the supplies of permeant fluid used should be de-aired. Air coming out of solution in the sample can significantly reduce the measured fluid conductivity. Deairing can be achieved by boiling the water supply under a vacuum, bubbling helium gas through the supply, or both.

2.4.1.1 Significant reductions in hydraulic conductivity can also occur in the growth and multiplication of microorganisms present in the sample. If it is desirable to prevent such growth, a bactericide or fungicide, such as 2000 ppm formaldehyde or 1000 ppm phenol (Olsen and Daniel, 1981), can be added to the fluid supply.

2.4.1.1 Fluid used for determining hydraulic conductivity in the laboratory should never be distilled water. Native ground water from the aquifer underlying the sampled area or water prepared to simulate the native ground water chemistry should be used.

2.4.2 **Pressure and Fluid Potential Measurement:** The equations in this report are all dimensionally correct; that is, any consistent set of units may be used for length, mass, and time. Consequently, measurements of pressure and/or fluid potential using pressure gages and manometers must be reduced to the consistent units used before applying either Equation 8 or 9. Pressures or potentials should be measured to within a few tenths of one percent of the gradient applied across the sample.

2.5 Constant-head test with conventional permeameter:

2.5.1 **Applicability:** This method covers the determination of the hydraulic conductivity of soils by a constant-head method using a conventional permeameter. This method is recommended for disturbed coarse-grained soils. If this method is to be used for fine-grained soils, the testing time may be prohibitively long. This method was taken from the Engineering and Design, Laboratory Soils Testing Manual (U.S. Army, 1980). It parallels ASTM Method D2434-68 (ASTM,1978). The ASTM

method gives extensive discussion of sample preparation and applicability and should be reviewed before conducting constant-head tests. Lambe (1951) provides additional information on sample preparation and equipment procedures.

2.5.2 **Apparatus:** The apparatus is shown schematically in Figure 3. It consists of the following:

1. A permeameter cylinder having a diameter at least 8 times the diameter of the largest particle of the material to be tested;
2. Constant-head filter tank;
3. Perforated metal disks and circular wire to support the sample;
4. Filter materials such as Ottawa sand, coarse sand, and gravel of various gradations;
5. Manometers connected to the top and bottom of the sample;
6. Graduated cylinder, 100-mL capacity;
7. Thermometer;
8. Stop watch;
9. Deaired water;
10. Balance sensitive to 0.1 gram; and
11. Drying oven.

2.5.3 **Sample preparation:**

1. Oven-dry the sample. Allow it to cool, and weigh to the nearest 0.1 g. Record the oven-dry weight of material. The amount of material should be sufficient to provide a specimen in the permeameter having a minimum length of about one to two times the diameter of the specimen.
2. Place a wire screen, with openings small enough to retain the specimen, over a perforated disk near the bottom of the permeameter above the inlet. The screen opening should be approximately equal to the 10 percent size of the specimen.
3. Allow deaired water to enter the water inlet of the permeameter to a height of about 1/2 in. above the bottom of the screen, taking care that no air bubbles are trapped under the screen.

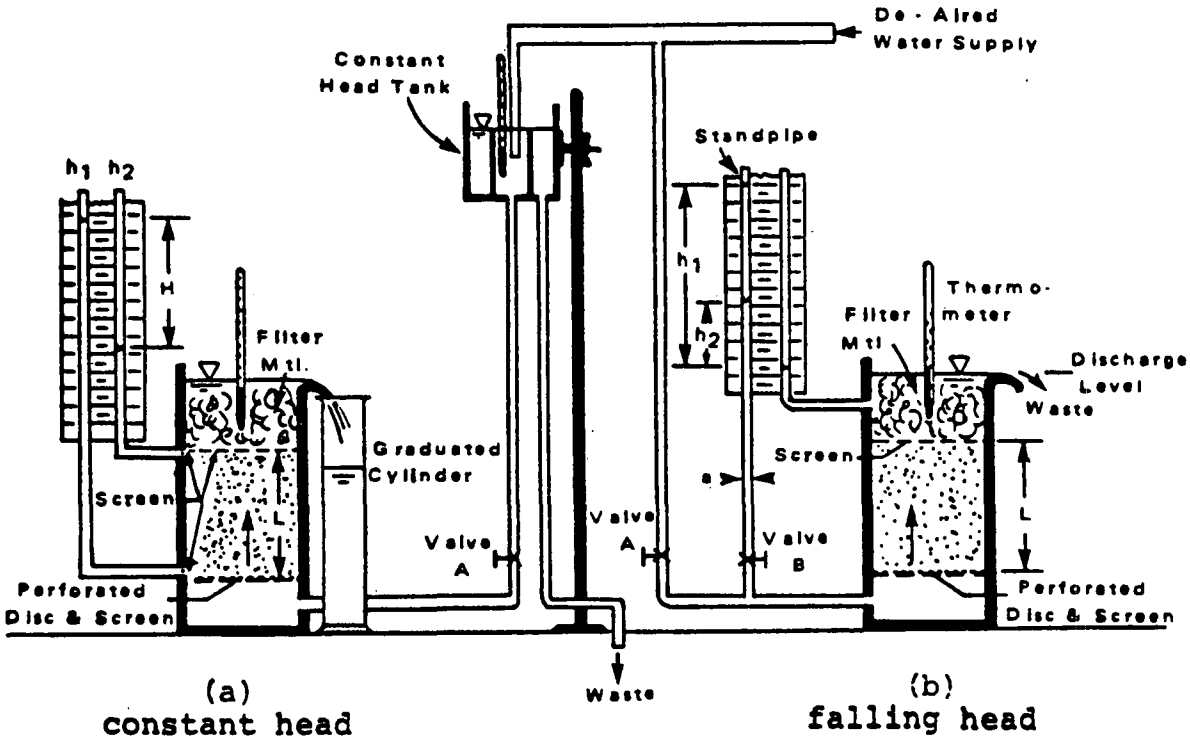


Figure 3.-- Apparatus setup for the constant head (a) and falling head (b) methods.

4. Mix the material thoroughly and place in the permeameter to avoid segregation. The material should be dropped just at the water surface, keeping the water surface about 1/2 in. above the top of the soil during placement. A funnel or a spoon is convenient for this purpose.

5. The placement procedure outlined above will result in a saturated specimen of uniform density although in a relatively loose condition. To produce a higher density in the specimen, the sides of the permeameter containing the soil sample are tapped uniformly along its circumference and length with a rubber mallet to produce an increase in density; however, extreme caution should be exercised so that fines are not put into suspension and segregated within the sample. As an alternative to this procedure, the specimen may be placed using an appropriate sized funnel or spoon. Compacting the specimen in layers is not recommended, as a film of dust which might affect the permeability results may be formed at the surface of the compacted layer. After placement, apply a vacuum to the top of the specimen and permit water to enter the evacuated specimen through the base of the permeameter.

6. After the specimen has been placed, weigh the excess material, if any, and the container. The specimen weight is the difference between the original weight of sample and the weight of the excess material. Care must be taken so that no material is lost during placement of the specimen. If there is evidence that material has been lost, oven-dry the specimen and weigh after the test as a check.

7. Level the top of the specimen, cover with a wire screen similar to that used at the base, and fill the remainder of the permeameter with a filter material.

8. Measure the length of the specimen, inside diameter of the permeameter, and distance between the centers of the manometer tubes (L) where they enter the permeameter.

2.5.4 **Test procedure:**

1. Adjust the height of the constant-head tank to obtain the desired hydraulic gradient. The hydraulic gradient should be selected so that the flow through the specimen is laminar. Hydraulic gradients ranging from 0.2 to 0.5 are recommended. Too high a hydraulic gradient may cause turbulent flow and also result in piping of soils. In general, coarser soils require lower hydraulic gradients. See Section 1.5 for further discussion of excessive gradients.

2. Open valve A (see Figure 3a) and record the initial piezometer readings after the flow has become stable. Exercise care in building up heads in the permeameter so that the specimen is not disturbed.

3. After allowing a few minutes for equilibrium conditions to be reached, measure by means of a graduated cylinder the quantity of discharge corresponding to a given time interval. Measure the piezometric heads (h_1 and h_2) and the water temperature in the permeameter.

4. Record the quantity of flow, piezometer readings, water temperature, and the time interval during which the quantity of flow was measured.

2.5.5 **Calculations:** By plotting the accumulated quantity of outflow versus time on rectangular coordinate paper, the slope of the linear portion of the curve can be determined, and the hydraulic conductivity can be calculated using Equation (8). The value of h in Equation (8) is the difference between h_1 and h_2.

2.6 Falling-head test with conventional permeameter:

2.6.1 **Applicability:** The falling-head test can be used for all soil types, but is usually most widely applicable to materials having low permeability. Compacted, remolded, fine-grained soils can be tested with this method. This method presented is taken from the Engineering and Design, Laboratory Soils Testing Manual (U.S. Army, 1980).

2.6.2 **Apparatus:** The schematic diagram of the falling-head permeameter is shown in Figure 3b. The permeameter consists of the following equipment:

1. Permeameter cylinder, a transparent acrylic cylinder having a diameter at least 8 times the diameter of the largest particles;

2. Porous disk;

3. Wire screen;

4. Filter materials;

5. Manometer;

6. Timing device; and

2.6.3 **Sample Preparation:** Sample preparation for coarse-grained soils is similar to that described previously in Section 2.4.3. For fine-grained soils, samples are compacted to the desired density using methods described in ASTM Method D698-70.

2.6.4 **Test Procedure:**

1. Measure and record the height of the specimen, L, and the cross-sectional area of the specimen, A.

2. With valve B open (see Figure 3b), crack valve A, and slowly bring the water level up to the discharge level of the permeameter.

3. Raise the head of water in the standpipe above the discharge level of the permeameter. The difference in head should not result in an excessively high hydraulic gradient during the test. Close valves A and B.

4. Begin the test by opening valve B. Start the timer. As the water flows through the specimen, measure and record the height of water in the standpipe above the discharge level, h_1, at time t_1, and the height of water above the discharge level, h_2 at time t_2.

2.6.5 **Calculations**. From the test data, plot the logarithm of head versus time on rectangular coordinate paper, or use semi-log paper. The slope of the linear part of the curve is used to determine $\log_{10}(h_1/h_2)/t$. Calculate the hydraulic conductivity using Equation (9).

2.7 Modified compaction permeameter method:

2.7.1 **Applicability:** This method can be used to determine the hydraulic conductivity of a wide range of materials. The method is generally used for remolded fine-grained soils. The method is generally used under constant-head conditions. The method was taken from Anderson and Brown, 1981, and EPA (1980). It should be noted that this method method of Section 2.9.

2.7.2 **Apparatus:** The apparatus is shown in Figure 4 and consists of equipment and accessories as follows:

1. Soil chamber, a compaction mold having a diameter 8 times larger than the diameter of the largest particles (typically, ASTM standard mold, Number CN405, is used);

2. Fluid chamber, a compaction mold sleeve having the same diameter as the soil chamber;

3. 2-kg hammer;

4. Rubber rings used for sealing purposes;

5. A coarse porous stone having higher permeability than the tested sample;

6. Regulated source of compressed air; and

7. Pressure gage or manometer to determine the pressure on the fluid chamber.

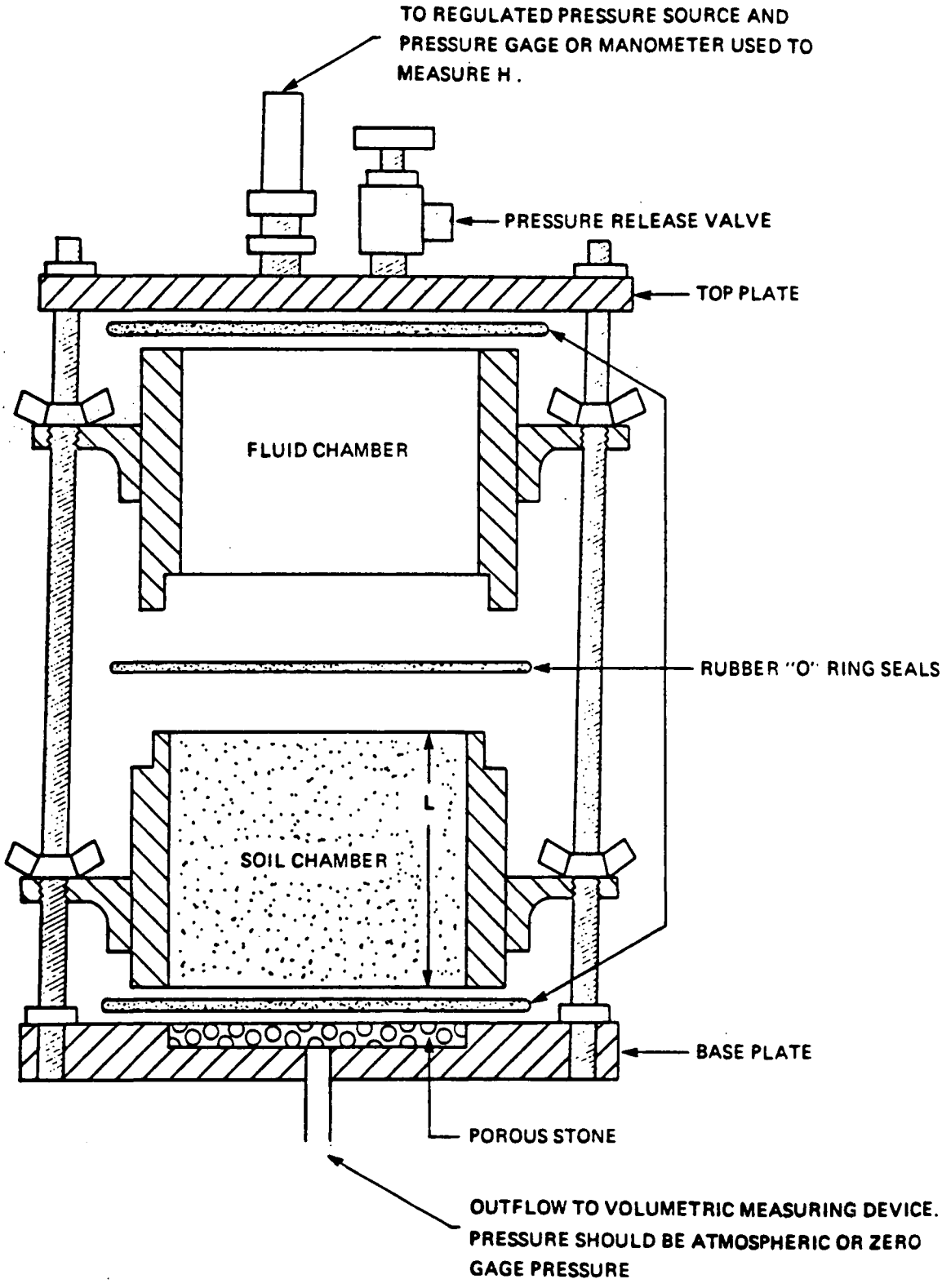


Figure 4.--Modified compaction permeameter. Note: h in Equation 8 is the difference between the regulated inflow pressure and the outflow pressure. Source: Anderson and Brown, 1981.

2.7.3 **Sample preparation:**

1. Obtain sufficient representative soil sample. Air dry the sample at room temperature. Do not oven dry.

2. Thoroughly mix the selected representative sample with water to obtain a desired moisture content.

3. Compact the sample to the desired density within the mold using the method described as part of ASTM Method D698-70.

4. Level the surface of the compacted sample with straight edge, weigh and determine the density of the sample.

5. Measure the length and diameter of the sample.

6. Assemble the apparatus, make sure that there are no leaks, and then connect the pressure line to the apparatus.

2.7.4 **Test procedure:**

1. Place sufficient volume of water in the fluid chamber above the soil chamber.

2. Apply air pressure gradually to flush water through the sample until no air bubbles in the outflow are observed. For fine-grained soils, the saturation may take several hours to several days, depending on the applied pressure.

3. After the sample is saturated, measure and record the quantity of outflow versus time.

4. Record the pressure reading (h) on the top of the fluid chamber when each reading is made.

5. Plot the accumulated quantity of outflow versus time on rectangular coordinate paper.

6. Stop taking readings as soon as the linear position of the curve is defined.

2.7.5 **Calculations:** The hydraulic conductivity can be calculated using Equation (8).

2.8 Triaxial-cell method with back pressure:

2.8.1 **Applicability:** This method is applicable for all soil types, but especially for fine-grained, compacted, cohesive soils in which full fluid saturation of the sample is difficult to achieve. Normally, the test is run under constant-head conditions.

2.8.2 **Apparatus:** The apparatus is similar to conventional triaxial apparatus. The schematic diagram of this apparatus is shown in Figure 5.

2.8.3 **Sample preparation:** Disturbed or undisturbed samples can be tested. Undisturbed samples must be trimmed to the diameter of the top cap and base of the triaxial cell. Disturbed samples should be prepared in the mold using either kneading compaction for fine-grained soils, or by the pouring and vibrating method for coarse-grained soils, as discussed in Section 2.5.3.

2.8.4 **Test procedure:**

1. Measure the dimensions and weight of the prepared sample.

2. Place one of the prepared specimens on the base.

3. Place a rubber membrane in a membrane stretcher, turn both ends of the membrane over the ends of the stretcher, and apply a vacuum to the stretcher. Carefully lower the stretcher and membrane over the specimen. Place the specimen and release the vacuum on the membrane stretcher. Turn the ends of the membrane down around the base and up around the specimen cap and fasten the ends with O-rings.

4. Assemble the triaxial chamber and place it in position in the loading device. Connect the tube from the pressure reservoir to the base of the triaxial chamber. With valve C (see Figure 5) on the pressure reservoir closed and valves A and B open, increase the pressure inside the reservoir, and allow the pressure fluid to fill the triaxial chamber. Allow a few drops of the pressure fluid to escape through the vent valve (valve B) to insure complete filling of the chamber with fluid. Close valve A and the vent valve.

5. Place saturated filter paper disks having the same diameter as that of the specimen between the specimen and the base and cap; these disks will also facilitate removal of the specimen after the test. The drainage lines and the porous inserts should be completely saturated with deaired water. The drainage lines should be as short as possible and made of thick-walled, small-bore tubing to insure minimum elastic changes in volume due to changes in pressure. Valves in the drainage lines (valves E, F, and G in Figure 5) should preferably be of a type which will cause no discernible change of internal volume when operated. While mounting the specimen in the compression chamber, care should be exercised to avoid entrapping any air beneath the membrane or between the specimen and the base and cap.

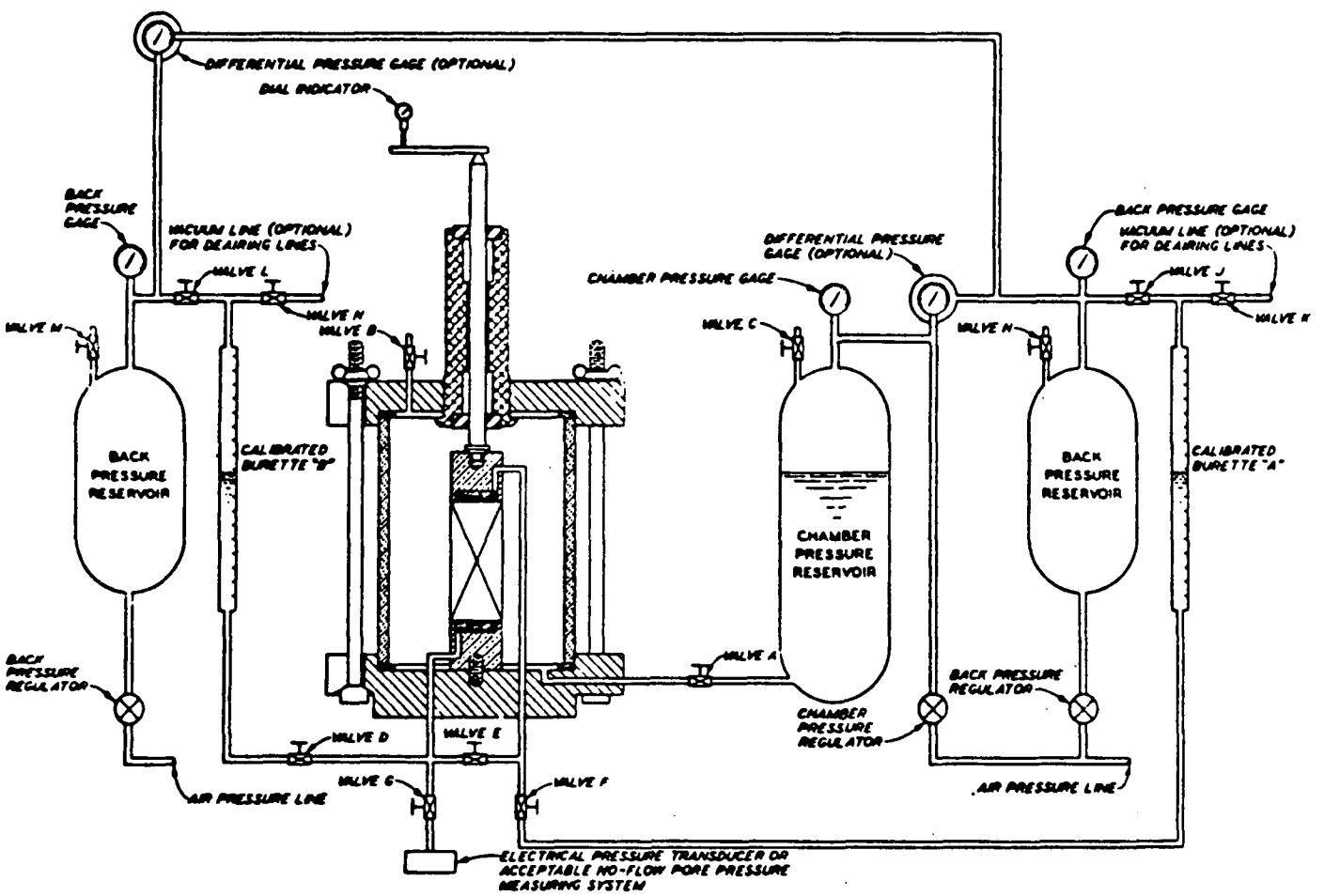


Figure 5.--Schematic diagram of typical triaxial compression apparatus for hydraulic conductivity tests with back pressure.
Source: U.S. Army Corps of Engineers, 1970

6. For ease and uniformity of saturation, as well as to allow volume changes during consolidation to be measured with the burette, specimens should be completely saturated before any appreciable consolidation is permitted; therefore, the difference between the chamber pressure and the back pressure should not exceed 5 psi during the saturation phase. To insure that a specimen is not prestressed during the saturation phase, the back pressure must be applied in small increments, with adequate time between increments to permit equalization of pore water pressure throughout the specimen.

7. With all valves closed, adjust the pressure regulators to a chamber pressure of about 7 psi and a back pressure of about 2 psi. Now open valve A to apply the preset pressure to the chamber fluid and simultaneously open valve F to apply the back pressure through the specimen cap. Immediately open valve G and read and record the pore pressure at the specimen base. When the measured pore pressure becomes essentially constant, close valves F and G and record the burette reading.

8. Using the technique described in Step 3, increase the chamber pressure and the back pressure in increments, maintaining the back pressure at about 5 psi less than the chamber pressure. The size of each increment might be 5, 10, or even 20 psi, depending on the compressibility of the soil specimen and the magnitude of the desired consolidation pressure. Open valve G and measure the pore pressure at the base immediately upon application of each increment of back pressure and observe the pore pressure until it becomes essentially constant. The time required for stabilization of the pore pressure may range from a few minutes to several hours depending on the permeability of the soil. Continue adding increments of chamber pressure and back pressure until, under any increment, the pore pressure reading equals the applied back pressure immediately upon opening valve G.

9. Verify the completeness of saturation by closing valve F and increasing the chamber pressure by about 5 psi. The specimen shall not be considered completely saturated unless the increase in pore pressure immediately equals the increase in chamber pressure.

10. When the specimen is completely saturated, increase the chamber pressure with the drainage valves closed to attain the desired effective consolidation pressure (chamber pressure minus back pressure). At zero elapsed time, open valves E and F.

11. Record time, dial indicator reading, and burette reading at elapsed times of 0, 15, and 30 sec, 1, 2, 4, 8, and 15 min, and 1, 2, 4, and 8 hr, etc. Plot the dial indicator readings and

burette readings on an arithmetic scale versus elapsed time on a log scale. When the consolidation curves indicate that primary consolidation is complete, close valves E and F.

12. Apply a pressure to burette B greater than that in burette A. The difference between the pressures in burettes B and A is equal to the head loss (h); h divided by the height of the specimen after consolidation (L) is the hydraulic gradient. The difference between the two pressures should be kept as small as practicable, consistent with the requirement that the rate of flow be large enough to make accurate measurements of the quantity of flow within a reasonable period of time. Because the difference in the two pressures may be very small in comparison to the pressures at the ends of the specimen, and because the head loss must be maintained constant throughout the test, the difference between the pressures within the burettes must be measured accurately; a differential pressure gage is very useful for this purpose. The difference between the elevations of the water within the burettes should also be considered (1 in. of water = 0.036 psi of pressure).

13. Open valves D and F. Record the burette readings at any zero elapsed time. Make readings of burettes A and B and of temperature at various elapsed times (the interval between successive readings depends upon the permeability of the soil and the dimensions of the specimen). Plot arithmetically the change in readings of both burettes versus time. Continue making readings until the two curves become parallel and straight over a sufficient length of time to determine accurately the rate of flow as indicated by the slope of the curves.

2.8.5 **Calculations:** The hydraulic conductivity can be calculated using Equation (8).

2.9 Pressure-chamber permeameter method:

2.9.1 **Applicability:** This method can be used to determine hydraulic conductivity of a wide range of soils. Undisturbed and disturbed samples can be tested under falling-head conditions using this method. This method is also applicable to both coarse- and fine-grained soils, including remolded, fine-grained materials.

2.9.2 **Apparatus:** The apparatus, shown in Figure 6, consists of

1. Pressure chamber;

2. Standpipe;

3. Specimen cap and base; and

4. Coarse porous plates.

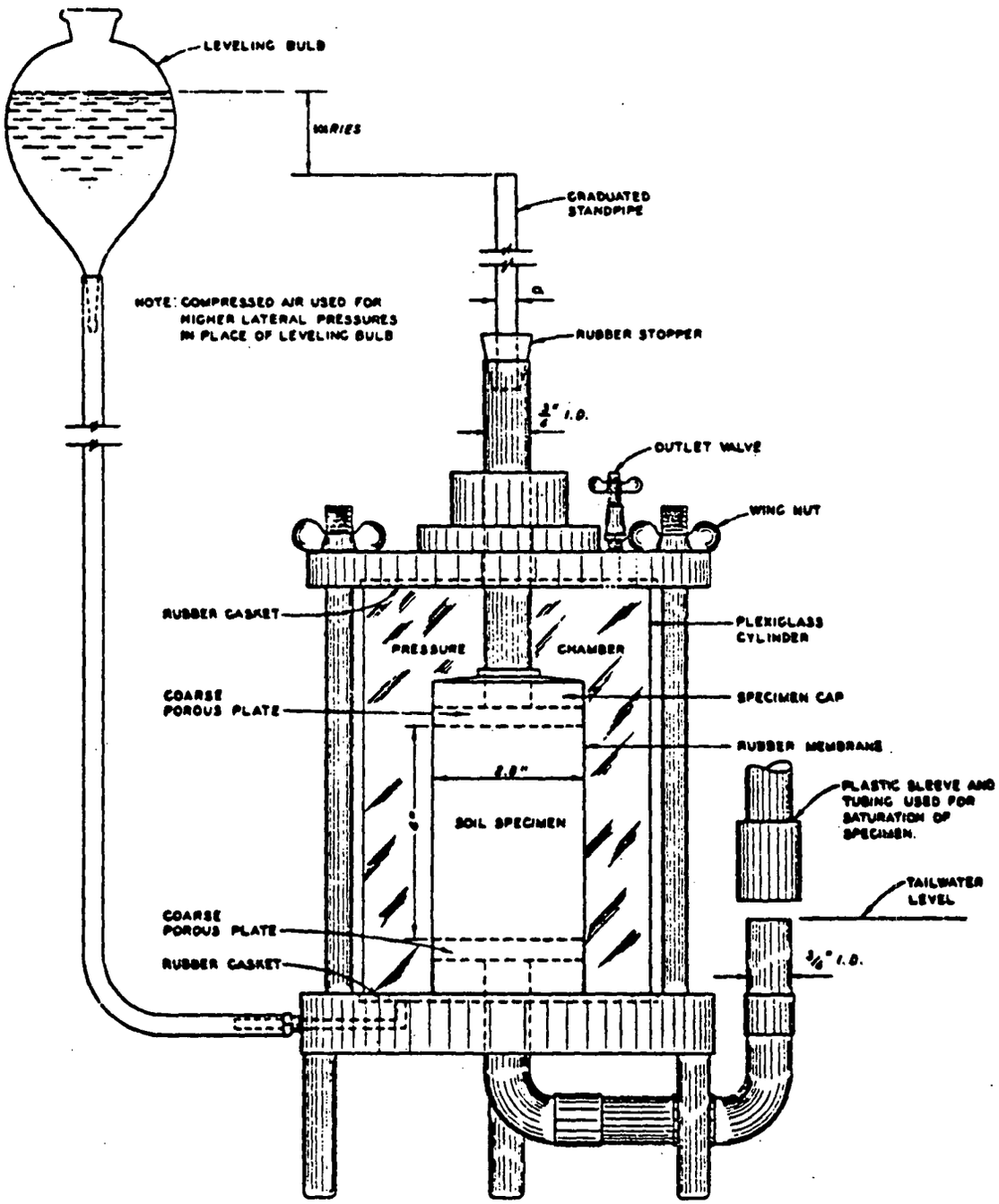


Figure 6.--Pressure chamber for hydraulic conductivity.
Source: U.S. Army Corps of Engineers, 1980.

The apparatus is capable of applying confining pressure to simulate field stress conditions.

2.9.3 **Sample preparation:** The sample preparation of disturbed and undisturbed conditions can be prepared in the chamber and enclosed within the rubber membrane, as discussed in Section 2.8.4.

2.9.4 **Test procedure:**

1. By adjusting the leveling bulb, a confining pressure is applied to the sample such that the stress conditions represent field conditions. For higher confining pressure, compressed air may be used.

2. Allow the sample to consolidate under the applied stress until the end of primary consolidation.

3. Flush water through the sample until no indication of air bubbles is observed. For higher head of water, compressed air may be used.

4. Adjust the head of water to attain a desired hydraulic gradient.

5. Measure and record the head drop in the standpipe along with elapsed time until the plot of logarithm of head versus time is linear for more than three consecutive readings.

2.9.5 **Calculations:** The hydraulic conductivity can be determined using Equation (9).

2.10 Sources of error for laboratory test for hydraulic conductivity: There are numerous potential sources of error in laboratory tests for hydraulic conductivity. Fixed-wall permeameters may have problems with sidewall leakage, causing higher values of hydraulic conductivity. Flexible-membrane permeameters may yield misleadingly low values for hydraulic conductivity when testing with a leachate that causes contraction and shrinkage cracks in the sample because the membrane shrinks with the sample. Table B summarizes some potential errors that can occur. Olsen and Daniel (1981) provide a more detailed explanation of sources of these errors and methods to minimize them. If the hydraulic conductivity does not fall within the expected range for the soil type, as given in Table C, the measurement should be repeated after checking the source of error in Table B.

TABLE B

SUMMARY OF PUBLISHED DATA ON POTENTIAL ERRORS
IN USING DATA FROM
LABORATORY PERMEABILITY TESTS ON SATURATED SOILS

Source of Error (References)	Measured K Too Low or Too High?
1. Voids formed in sample preparation (Olsen and Daniel, 1981).	High
2. Smear zone formed during trimming (Olsen and Daniel, 1981).	Low
3. Use of distilled water as a permeant (Fireman, 1944; and Wilkinson, 1969).	Low
4. Air in sample (Johnson, 1954)	Low
5. Growth of micro-organisms (Allison, 1947).	Low
6. Use of excessive hydraulic gradient (Schwartzendruber, 1968; and Mitchell and Younger, 1967).	Low or High
7. Use of temperature other than the test temperature.	Varies
8. Ignoring volume change due to stress change, with no confining pressure used.	High
9. Performing laboratory rather than in-situ tests (Olsen and Daniel, 1981).	Usually Low
10. Impedance caused by the test apparatus, including the resistance of the screen or porous stone used to support the sample.	Low

TABLE C

HYDRAULIC CONDUCTIVITIES ESTIMATED FROM GRAIN-SIZE DESCRIPTIONS
(In Feet Per Day)

Grain-Size Class or Range From Sample Description	Degree of Sorting			Silt Content		
	Poor	Moderate	Well	Slight	Moderate	High
Fine-Grained Materials						
Clay				Less than .001		
Silt, clayey				1 - 4		
Silt, slightly sandy				5		
Silt, moderately sandy				7 - 8		
Silt, very sandy				9 - 11		
Sandy silt				11		
Silty sand				13		
Sands and gravels(1)						
Very fine sand	13	20	27	23	19	13
Very fine to fine sand	27	27	-	24	20	13
Very fine to medium sand	36	41-47	-	32	27	21
Very fine to coarse sand	48	-	-	40	31	24
Very fine to very coarse sand	59	-	-	51	40	29
Very fine sand to fine gravel	76	-	-	67	52	38
Very fine sand to medium gravel	99	-	-	80	66	49
Very fine sand to coarse gravel	128	-	-	107	86	64
Fine sand	27	40	53	33	27	20
Fine to medium sand	53	67		48	39	30
Fine to coarse sand	57	65-72	-	53	43	32
Fine to very coarse sand	70	-	-	60	47	35
Fine sand to fine gravel	88	-	-	74	59	44
Fine sand to medium gravel	114	-	-	94	75	57
Fine sand to coarse gravel	145	-	-	107	87	72
Medium sand	67	80	94	64	51	40
Medium to coarse sand	74	94	-	72	57	42
Medium to very coarse sand	84	98-111	-	71	61	49
Medium sand to fine gravel	103	-	-	84	68	52
Medium sand to medium gravel	131	-	-	114	82	66
Medium sand to coarse gravel	164	-	-	134	108	82
Coarse sand	80	107	134	94	74	53
Coarse to very coarse sand	94	134	-	94	75	57
Coarse sand to fine gravel	116	136-156	-	107	88	68
Coarse sand to medium gravel	147	-	-	114	94	74
Coarse sand to coarse gravel	184	-	-	134	100	92

(1) Reduce by 10 percent if grains are subangular.
Source: Lappala (1978).

(continued)

TABLE C (Continued)

Grain-Size Class or Range From Sample Description	Degree of Sorting Poor	Moderate	Well	Silt Content Slight	Moderate	High
Sands and Gravels(1)						
Very coarse sand	107	147	187	114	94	74
Very coarse sand to fine gravel	134	214	-	120	104	87
Very coarse sand to medium gravel	1270	199-227	-	147	123	99
Very coarse sand to coarse gravel	207	-	-	160	132	104
Fine gravel	160	214	267	227	140	107
Fine to medium gravel	201	334	-	201	167	134
Fine to coarse gravel	245	289-334	-	234	189	144
Medium gravel	241	231	401	241	201	160
Medium to coarse gravel	294	468	-	294	243	191
Coarse gravel	334	468	602	334	284	234

(1) Reduce by 10 percent if grains are subangular.
Source: Lappala (1978).

2.11 Leachate conductivity using laboratory methods: Many primary and secondary leachates found at disposal sites may be nonaqueous liquids or aqueous fluids of high ionic strength. These fluids may significantly alter the intrinsic permeability of the porous medium. For example, Anderson and Brown (1981) have demonstrated increases in hydraulic conductivity of compacted clays of as much as two orders of magnitude after the passage of a few pore volumes of a wide range of organic liquids. Consequently, the effects of leachate on these materials should be evaluated by laboratory testing. The preceding laboratory methods can all be used to determine leachate conductivity by using the following guidelines.

2.11.1 **Applicability:** The determination of leachate conductivity may be required for both fine-grained and coarse-grained materials. Leachates may either increase or decrease the hydraulic conductivity. Increases are of concern for compacted clay liners, and decreases are of concern for drain materials. The applicability sections of the preceding methods should be used for selecting an appropriate test for leachate conductivity. The use of the modified compaction method (Section 2.7) for determining leachate conductivity is discussed extensively in EPA Publication SW870 (EPA 1980).

2.11.2 **Leachate used:** A supply of leachate must be obtained that is as close in chemical and physical properties to the anticipated leachate at the disposal site as possible. Methods for obtaining such leachate are beyond the scope of this report. However, recent publications by EPA (1979) and Conway and Malloy (1981) give methodologies for simulating the leaching environment to obtain such leachate. Procedures for deairing the leachate supply are given in Section 2.4. The importance of preventing bacterial growth in leachate tests will depend on the expected conditions at the disposal site. The chemical and physical properties that may result in corrosion, dissolution, or encrustation of laboratory hydraulic conductivity apparatus should be determined prior to conducting a leachate conductivity test. Properties of particular importance are the pH and the vapor pressure of the leachate. Both extremely acidic and basic leachates may corrode materials. In general, apparatus for leachate conductivity tests should be constructed of inert materials, such as acrylic plastic, nylon, or Teflon. Metal parts that might come in contact with the leachate should be avoided. Leachates with high vapor pressures may require special treatment. Closed systems for fluid supply and pressure measurement, such as those in the modified triaxial-cell methods, should be used.

2.11.3 **Safety:** Tests involving the use of leachates should be conducted under a vented hood, and persons conducting the tests should wear appropriate protective clothing and eye protection. Standard laboratory safety procedures such as those as given by Manufacturing Chemists Association (1971) should be followed.

2.11.4 **Procedures:** The determination of leachate conductivity should be conducted immediately following the determination of hydraulic

conductivity (Anderson and Brown, 1981). This procedure maintains fluid saturation of the sample, and allows a comparison of the leachate and hydraulic conductivities under the same test conditions. This procedure requires modifications of test operations as described below.

2.11.5 **Apparatus:** In addition to a supply reservoir for water as shown in Figures 3 through 6, a supply reservoir for leachate is required. Changing the inflow to the test cell from water to leachate can be accomplished by providing a three-way valve in the inflow line that is connected to each of the reservoirs.

2.11.6 **Measurements:** Measurements of fluid potential and outflow rates are the same for leachate conductivity and hydraulic conductivity. If the leachate does not alter the intrinsic permeability of the sample, the criteria for the time required to take measurements is the same for leachate conductivity tests as for hydraulic conductivity tests. However, if significant changes occur in the sample by the passage of leachate, measurements should be taken until either the shape of a curve of conductivity versus pore volume can be defined, or until the leachate conductivity exceeds the applicable design value for hydraulic conductivity.

2.11.7 **Calculations:** If the leachate conductivity approaches a constant value, Equations (8) and (9) can be used. If the conductivity changes continuously because of the action of the leachate, the following modifications should be made. For constant-head tests, the conductivity should be determined by continuing a plot of outflow volume versus time for the constant rate part of the test conducted with water. For falling-head tests, the slope of the logarithm of head versus time should be continued.

2.11.7.1 If the slope of either curve continues to change after the flow of leachate begins, the leachate is altering the intrinsic permeability of the sample. The leachate conductivity in this case is not a constant. In this case, values of the slope of the outflow curve to use in Equation (8) or (9) must be taken as the tangent to the appropriate outflow curve at the times of measurement.

3.0 FIELD METHODS

This section discusses methods available for the determination of fluid conductivity under field conditions. As most of these tests will use water as the testing fluid, either natural formation water or water added to a borehole or piezometer, the term hydraulic conductivity will be used for the remainder of this section. However, if field tests are run with leachate or other fluids, the methods are equally applicable.

The location of wells, selection of screened intervals, and the appropriate tests that are to be conducted depend upon the specific site under

investigation. The person responsible for such selections should be a qualified hydrogeologist or geotechnical engineer who is experienced in the application of established principles of contaminant hydrogeology and ground water hydraulics. The following are given as general guidelines.

1. The bottom of the screened interval should be below the lowest expected water level.

2. Wells should be screened in the lithologic units that have the highest probability of either receiving contaminants or conveying them down gradient.

3. Wells up gradient and down gradient of sites should be screened in the same lithologic unit.

Standard reference texts on ground water hydraulics and contaminant hydrogeology that should be consulted include: Bear (1972), Bouwer (1978), Freeze and Cherry (1979), Stallman (1971), and Walton (1970).

The success of field methods in determining hydraulic conductivity is often determined by the design, construction, and development of the well or borehole used for the tests. Details of these methods are beyond the scope of this report; however, important considerations are given in Sections 3.1 and 3.2. Detailed discussions of well installation, construction, and development methods are given by Bouwer, pp. 160-180 (1978), Acker (1974), and Johnson (1972).

The methods for field determination of hydraulic conductivity are restricted to well or piezometer type tests applicable below existing water tables. Determinations of travel times of leachate and dissolved solutes above the water table usually require the application of unsaturated flow theory and methods which are beyond the scope of this report.

3.1 Well-construction considerations: The purpose of using properly constructed wells for hydraulic conductivity testing is to assure that test results reflect conditions in the materials being tested, rather than conditions caused by well construction. In all cases, diagrams showing all details of the actual well or borehole constructed for the test should be made. Chapter 3 of the U.S. EPA, RCRA Ground Water Monitoring Technical Enforcement Guidance Document (TEGD) should be consulted.

3.1.1 **Well installation methods:** Well installation methods are listed below in order of preference for ground water testing and monitoring. The order was determined by the need to minimize side-wall plugging by drilling fluids and to maximize the accurate detection of saturated zones. This order should be used as a guide, combined with the judgment of an experienced hydrogeologist in selecting a drilling method. The combined uses of wells for hydraulic conductivity testing, water-level monitoring, and water-quality sampling for organic contaminants were considered in arriving at the ranking.

1. Hollow-stem auger;

2. Cable tool;

3. Air rotary;

4. Rotary drilling with non-organic drilling fluids;

5. Air foam rotary; and

6. Rotary with organic-based drilling fluids.

Although the hollow stem-auger method is usually preferred for the installation of most shallow wells (less than 100 feet), care must be taken if the tested zone is very fine. Smearing of the borehole walls by drilling action can effectively seal off the borehole from the adjacent formation. Scarification can be used to remedy this.

3.1.2 **Wells requiring well screens:** Well screens placed opposite the interval to be tested should be constructed of materials that are compatible with the fluids to be encountered. Generally an inert plastic such as PVC is preferred for ground water contamination studies. The screen slot size should be determined to minimize the inflow of fine-grained material to the well during development and testing. Bouwer (1978) and Johnson (1972) give a summary of guidelines for sizing well screens.

3.1.2.1 The annulus between the well screen and the borehole should be filled with an artificial gravel pack or sand filter. Guidelines for sizing these materials are given by Johnson (1972). For very coarse materials, it may be acceptable to allow the materials from the tested zone to collapse around the screen forming a natural gravel pack.

3.1.2.2 The screened interval should be isolated from overlying and underlying zones by materials of low hydraulic conductivity. Generally, a short bentonite plug is placed on top of the material surrounding the screen, and cement grout is placed in the borehole to the next higher screened interval (in the case of multiple screen wells), or to the land surface for single screen wells.

3.1.2.3 Although considerations for sampling may dictate minimum casing and screen diameters, the recommended guideline is that wells to be tested by pumping, bailing, or injection in coarse-grained materials should be at least 4-inches inside diameter. Wells to be used for testing materials of low hydraulic conductivity by sudden removal or injection of a known volume of fluid should be constructed with as small a casing diameter as possible to maximize measurement resolution of fluid level changes. Casing sizes of 1.25 to 1.50 inches usually allow this resolution while enabling the efficient sudden withdrawal of water for these tests.

3.1.3 **Wells not requiring well screens:** If the zone to be tested is sufficiently indurated that a well screen and casing are not required to prevent caving in, it is preferable to use a borehole open to the zone to be tested. These materials generally are those having low to extremely low hydraulic conductivities. Consolidated rocks having high conductivity because of the presence of fractures and solution openings may also be completed without the use of a screen and gravel pack. Uncased wells may penetrate several zones for which hydraulic conductivity tests are to be run. In these cases, the zones of interest can be isolated by the use of inflatable packers.

3.2 Well development: For wells that are constructed with well screens and gravel packs, and for all wells in which drilling fluids have been used that may have penetrated the materials to be tested, adequate development of the well is required to remove these fluids and to remove the fine-grained materials from the zone around the well screen. Development is carried out by methods such as intermittent pumping, jetting with water, surging, and bailing. Adequate development is required to assure maximum communication between fluids in the borehole and the zone to be tested. Results from tests run in wells that are inadequately developed will include an error caused by loss of fluid potential across the undeveloped zone, and computed hydraulic conductivities will be lower than the actual value. Bouwer (1978) and Johnson (1975) give further details on well development including methods to determine when adequate development has occurred. The U.S. EPA TEGD should also be consulted.

3.3 Data interpretation and test selection considerations: Hydraulic conductivity may be determined in wells that are either cased or uncased as described in Section 3.1. The tests all involve disturbing the existing fluid potential in the tested zone by withdrawal from or injection of fluid into a well, either as a slug over an extremely short period of time, or by continuous withdrawal or injection of fluid. The hydraulic conductivity is determined by measuring the response of the water level or pressure in the well as a function of time since the start of the test. Many excellent references are available that give the derivation and use of the methods that are outlined below, including Bouwer (1978), Walton (1969), and Lohman (1972).

3.3.1 The selection of a particular test method and data analysis technique requires the consideration of the purposes of the test, and the geologic framework in which the test is to be run. Knowledge of the stratigraphic relationships of the zone to be tested and both overlying and underlying materials should always be used to select appropriate test design and data interpretation methods.

3.3.2 The equations given for all computational methods given here and in the above references are based on idealized models comprising layers of materials of different hydraulic conductivities. The water-level response caused by disturbing the system by the addition or removal of water can be similar for quite different systems. For example, the response of a water-table aquifer and a leaky, confined aquifer to

pumping can be very similar. Consequently, it is not considered acceptable practice to obtain data from a hydraulic conductivity test and interpret the type of hydraulic system present without supporting geologic evidence.

3.3.3 The primary use of hydraulic conductivity data from tests described subsequently will usually be to aid in siting monitoring wells for facility design as well as for compliance with Subpart F of Part 264. As such, the methods are abbreviated to provide guidance in determining hydraulic conductivity only. Additional analyses that may be possible with some methods to define the storage properties of the aquifer are not included. The U.S. EPA TEGD has an expanded discussion on the relationship between K tests and siting design (Chapter 1) and should be consulted.

3.3.4 The well test methods are discussed under the following two categories: 1) methods applicable to coarse-grained materials and tight to extremely tight materials under confined conditions; and 2) methods applicable to unconfined materials of moderate permeability. The single well tests integrate the effects of heterogeneity and anisotropy. The effects of boundaries such as streams or less permeable materials usually are not detectable with these methods because of the small portion of the geologic unit that is tested.

3.4 Single well tests: The tests for determining hydraulic conductivity with a single well are discussed below based on methods for confined and unconfined conditions. The methods are usually called slug tests because the test involves removing a slug of water instantaneously from a well and measuring the recovery of water in the well. The method was first developed by Hvorslev (1951), whose analysis did not consider the effect of fluid stored in the well. Cooper and others (1967) developed a method that considers well bore storage. However, their method only applied to wells that are open to the entire zone to be tested and that tap confined aquifers. Because of the rapid water-level response in coarse materials, the tests are generally limited to zones with a transmissivity of less than about 70 cm^2/sec (Lohman, 1972). The method has been extended to allow testing of extremely tight formations by Bredehoeft and Papadopulos (1980). Bouwer and Rice (1976) developed a method for analyzing slug tests for unconfined aquifers.

3.4.1 **Method for moderately permeable formations under confined conditions:**

3.4.1.1 Applicability: This method is applicable for testing zones to which the entire zone is open to the well screen or open borehole. The method usually is used in materials of moderate hydraulic conductivity which allow measurement of water-level response over a period of a hour to a few days. More permeable zones can be tested with rapid response water-level recording equipment. The method assumes that the tested zone is uniform in all radial directions from the test well. Figure 7 illustrates the test geometry for this method.

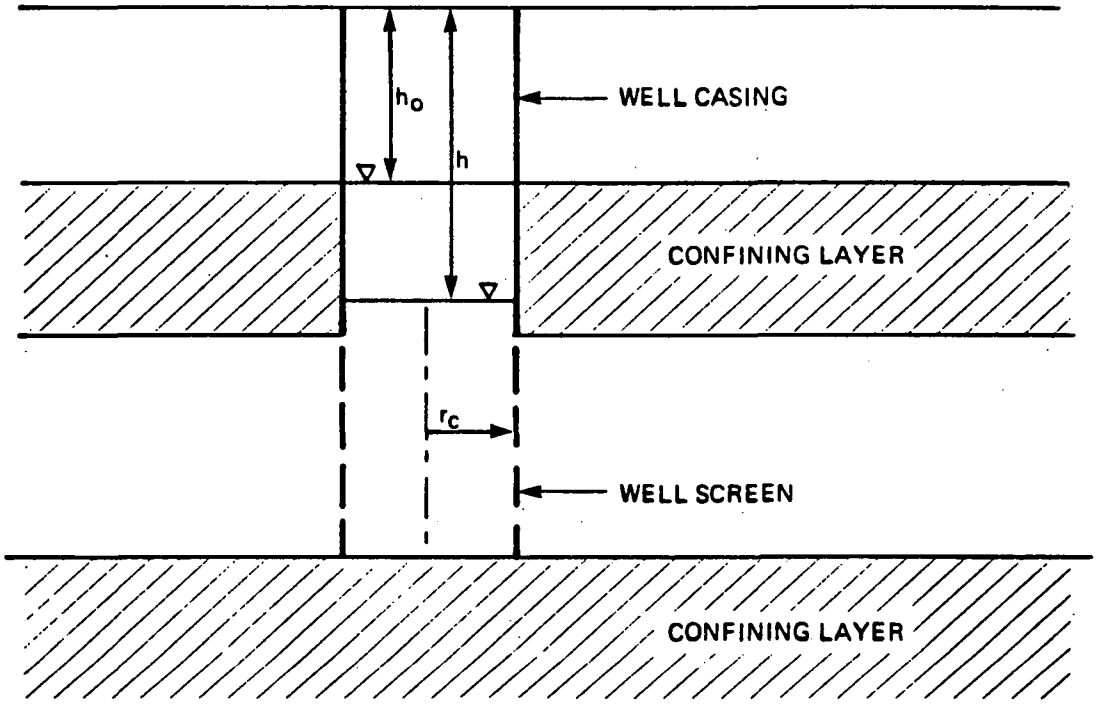


Figure 7.--Geometry and variable definition for slug tests in confined aquifers.

3.4.1.2 Procedures: The slug test is run by utilizing some method of removing or adding a known volume of water from the well bore in a very short time period and measuring the recovery of the water level in the well. The procedures are the same for both unconfined and confined aquifers. Water is most effectively removed by using a bailer that has been allowed to fill and stand in the well for a sufficiently long period of time so that any water-level disturbance caused by the insertion of the bailer will have reached equilibrium. In permeable materials, this recovery time may be as little as a few minutes. An alternate method of effecting a sudden change in water level is the withdrawal of a weighted float. The volume of water displaced can be computed using the known submersed volume of the float and Archimedes' principle (Lohman, 1972).

Water-level changes are recorded using either a pressure transducer and a strip chart recorder, a weighted steel tape, or an electric water-level probe. For testing permeable materials that approach or exceed 70 cm^2/sec, a rapid-response transducer/recorder system is usually used because essentially full recovery may occur in a few minutes. Because the rate of water-level response decays with time, water-level or pressure changes should be taken at increments that are approximately equally spaced in the logarithm of the time since fluid withdrawal. The test should be continued until the water level in the well has recovered to at least 85 percent of the initial pre-test value.

3.4.1.3 Calculations: Calculations for determining hydraulic conductivity for moderately permeable formations under confined conditions can be made using the following procedure:

1. Determine the transmissivity of the tested zone by plotting the ratio h/h_0 on an arithmetic scale against time since removal of water (t) on a logarithmic scale. The observed fluid potential in the well during the test as measured by water level or pressure is h, and the fluid potential before the instant of fluid withdrawal is h_0. The data plot is superimposed on type curves, such as those given by Lohman (1972), Plate 2, or plotted from Appendix A, with the h/h_0 and time axes coincident. The data plot is moved horizontally until the data fits one of the type curves. A value of time on the data plot corresponding to a dimensionless time (β) on the type curve plot is chosen, and the transmissivity is computed from the following:

$$T = \frac{\beta r_c^2}{t} \qquad (10)$$

where:

r_c is the radius of the casing (Lohman, p. 29 (1972)).

The type curves plotted using data in Appendix A are not to be confused with those commonly referred to as "Theis Curves" which are used for pumping tests in confined aquifers (Lohman, 1972). The type curve method is a general technique of determining aquifer parameters when the solution to the descriptive flow equation involves more than one unknown parameter. Although both the storage coefficient and transmissivity of the tested interval can be determined with the type curve method for slug tests, determination of storage coefficients is beyond the scope of this report. See Section 3.4.1.4 for further discussion of the storage coefficient.

If the data in Appendix A are used, a type curve for each value of α is prepared by plotting $F(\alpha,\beta)$ on the arithmetic scale and dimensionless time (β) on the logarithmic scale of semi-log paper.

2. Determine the hydraulic conductivity by dividing the transmissivity (T) calculated above by the thickness of the tested zone.

3.4.1.4 Sources of error: The errors that can arise in conducting slug tests can be of three types: those resulting from the well or borehole construction; measurement errors; and data analysis error.

Well construction and development errors: This method assumes that the entire thickness of the zone of interest is open to the well screen or boreholes and that flow is principally radial. If this is not the case, the computed hydraulic conductivity may be too high. If the well is not properly developed, the computed conductivity will be too low.

Measurement errors: Determining or recording the fluid level in the borehole and the time of measurement incorrectly can cause measurement errors. Water levels should be measured to an accuracy of at least 1 percent of the initial water-level change. For moderately permeable materials, time should be measured with an accuracy of fractions of minutes, and, for more permeable materials, the time should be measured in terms of seconds or fractions of seconds. The latter may require the use of a rapid-response pressure transducer and recorder system.

Data analysis errors: The type curve procedure requires matching the data to one of a family of type curves, described by the parameter , which is a measure of the storage in the well bore and aquifer. Papadopulos and others (1973) show that an error of two orders of magnitude in the selection of would result in an error of less than 30 percent in the value of transmissivity determined. Assuming no error in determining the thickness of the zone tested, this is equivalent to a 30 percent error in the hydraulic conductivity.

3.4.2 **Methods for extremely tight formations under confined conditions:**

3.4.2.1 Applicability: This test is applicable to materials that have low to extremely low permeability such as silts, clays, shales, and indurated lithologic units. The test has been used to determine hydraulic conductivities of shales of as low as 10^{-10} cm/sec.

3.4.2.2 Procedures: The test described by Bredehoeft and Papadopulos (1980) and modified by Neuzil (1982) is conducted by suddenly pressurizing a packed-off zone in a portion of a borehole or well. The test is conducted using a system such as shown in Figure 8. The system is filled with water to a level assumed to be equal to the prevailing water level. (This step is required if sufficiently large times have not elapsed since the drilling of the well to allow full recovery of water levels.) A pressure transducer and recorder are used to monitor pressure changes in the system for a period prior to the test to obtain pressure trends preceding the test. The system is pressurized by addition of a known volume of water with a high-pressure pump. The valve is shut and the pressure decay is monitored. Neuzil's modification uses two packers with a pressure transducer below the bottom packer to measure the pressure change in the cavity and one between the two packers to monitor any pressure change caused by leakage around the bottom packer.

3.4.2.3 Calculations: The modified slug test as developed by Bredehoeft and Papadopulos (1980) considered compressive storage of water in the borehole. These authors considered that the volume of the packed-off borehole did not change during the test and that all compressive storage resulted in compression of water under the pressure pulse. Neuzil (1980) demonstrated that under some test conditions this is not a valid assumption. The computational from either Lohman, Plate 2 (1972) or plotted from data given in Appendix A as described in Section 3.4.1.3. The values of time (t) and dimensionless time (β) are determined in the same manner as for the conventional tests. If compression of water only is considered, transmissivity is computed by replacing r_c by the quantity $(V_W C_W \rho_g/\pi)$ in Equation 10:

$$T = \frac{\beta(V_W\, C_W\, \rho_g/\pi)^2}{t} \qquad (10)$$

where:

V_W is the volume of water in the packed-off cavity, L^3;

C_W is the compressibility of water, LT^2M^{-1};

ρ is the density of water, ML^{-3}; and

g is the acceleration of gravity, LT^{-2}.

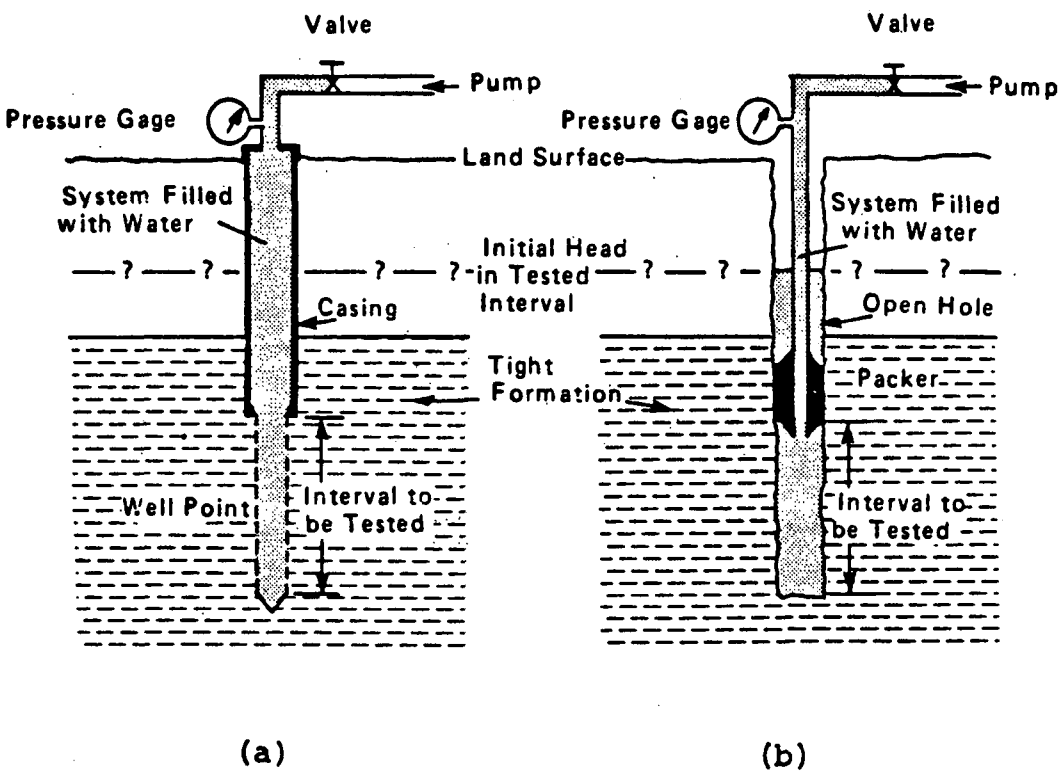


Figure 8.--Schematic diagram for pressurized slug test method in unconsolidated (a) and consolidated (b) materials. Source: Papadopulos and Bredehoeft, 1980.

If the compressive storage is altered by changing the volume of the packed-off cavity (V), then the combined compressibility of the water and the expansion of the cavity (C_o) is used. C_o is computed by measuring the volume of water injected during pressurization (ΔV) and the pressure change (ΔP) for the pressurization:

$$C_o = \frac{\Delta V}{V \Delta P} \tag{11}$$

(Neuzil, p. 440 (1982)). Use of C_o requires an accurate method of metering the volume of water injected and the volume of the cavity.

3.4.2.4 Sources of error: The types of errors in this method are the same as those for the conventional slug test. Errors may also arise by inaccurate determination of the cavity volume and volume of water injected. An additional assumption that is required for this method is that the hydraulic properties of the interval tested remain constant throughout the test. This assumption can best be satisfied by limiting the initial pressure change to a value only sufficiently large enough to be measured (Bredehoeft and Papadopulos, 1980).

3.4.3 **Methods for moderately permeable materials under unconfined conditions:**

3.4.3.1 Applicability: This method is applicable to wells that fully or partially penetrate the interval of interest (Figure 9). The hydraulic conductivity determined will be principally the value in the horizontal direction (Bouwer and Rice, 1976).

3.4.3.2 Procedures: A general method for testing cased wells that partly or fully penetrate aquifers that have a water table as the upper boundary of the zone to be tested was developed by Bouwer and Rice (1976). The geometry and dimensions that are required to be known for the method are shown in Figure 9. The test is accomplished by effecting a sudden change in fluid potential in the well by withdrawal of either a bailer or submerged float as discussed in Section 3.4.1.2. Water-level changes can be monitored with either a pressure transducer and recorder, a wetted steel tape, or an electric water-level sounder. For highly permeable formations, a rapid-response transducer and recorder system is required. The resolution of the transducer should be about 0.01 m.

3.4.3.3 Calculations: The hydraulic conductivity is calculated using the following equation from Bouwer and Rice (1976), in the notation of this report:

$$K = \frac{r_c^2 \ln \bar{R}/r_w}{2 L_e t} \ln \frac{Y_o}{Y} \tag{12}$$

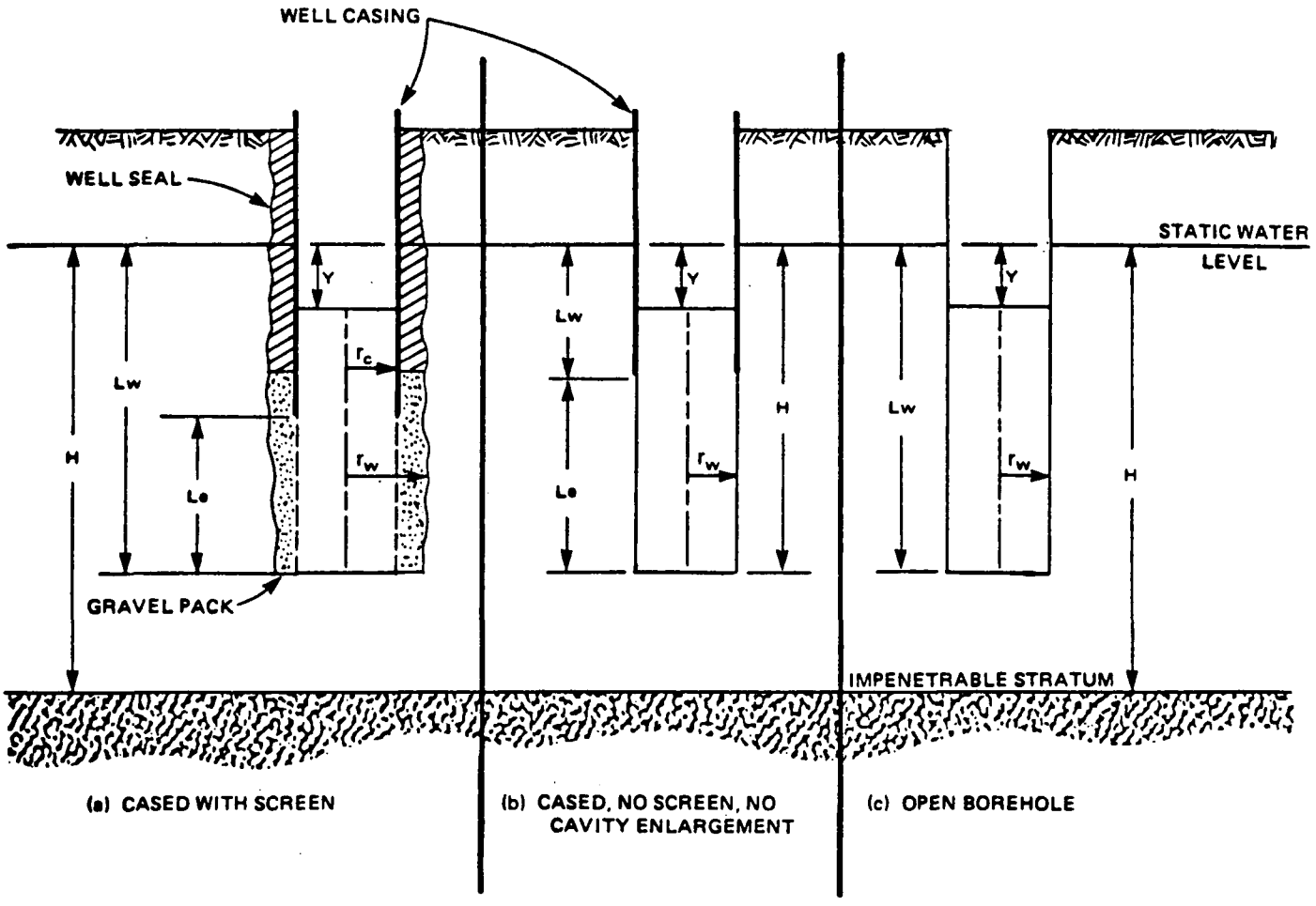


Figure 9.--Variable definitions for slug tests in unconfined materials. Cased wells are open at the bottom.

where r_c, r_w, L_e, t, Y, and K have been previously defined or are defined in Figure 8a. Y_o is the value of Y immediately after withdrawal of the slug of water. The term $\bar{R}$ is an effective radius for wells that do not fully penetrate the aquifer that is computed using the following equation given by Bouwer and Rice (1976):

$$\ln \frac{\bar{R}}{r_w} = \left\{ \frac{1.1}{\ln (L_w/r_w)} + \frac{A + B \ln[(H_o-L_w)/r_w]}{(L_e/r_w)} \right\}^{-1} \quad (13)$$

If the quantity $(H_o-L_w)/r_w)$ is larger than 6, a value of 6 should be used.

For wells that completely penetrate the aquifer, the following equation is used:

$$\ln \frac{\bar{R}}{r_w} = \left\{ \frac{1.1}{\ln (L_w/r_w)} + \frac{C}{L_e/r_w} \right\}^{-1} \quad (14)$$

(Bouwer, 1976). The values of the constants A, B, and C are given by Figure 10 (Bouwer and Rice, 1976).

For both cases, straight-line portions of plots of the logarithm of Y or Y_o/Y against time should be used to determine the slope, $(\ln Y_o/Y)/t$.

Additional methods for tests under unconfined conditions are summarized by Bower (1976) on pages 117-122. These methods are modifications of the cased-well method described above that apply either to an uncased borehole or to a well or piezometer in which the diameter of the casing and the borehole are the same (Figures 9b and 9c.)

3.4.3.4 Sources of error: The method assumes that flow of water from above is negligible. If this assumption cannot be met, the conductivities may be in error. Sufficient flow from the unsaturated zone by drainage would result in a high conductivity value. Errors caused by measuring water levels and recording time are similar to those discussed in Sections 3.4.1.4 and 3.4.2.4.

3.5 Multiple well tests: Hydraulic conductivity can also be determined by conventional pumping tests in which water is continuously withdrawn or injected using one well, and the water-level response is measured over time in or near more observation wells. The observation wells must be screened in the same strata as the injection or pumping well. These methods generally test larger portions of aquifers than the single well tests discussed in Section 3.4. For some circumstances these tests may be appropriate in obtaining data to use in satisfying requirements of Part 264 Subpart F. However, the large possibility for non-uniqueness in interpretation, problems involved in pumping contaminated fluids, and the expense of conducting such tests generally

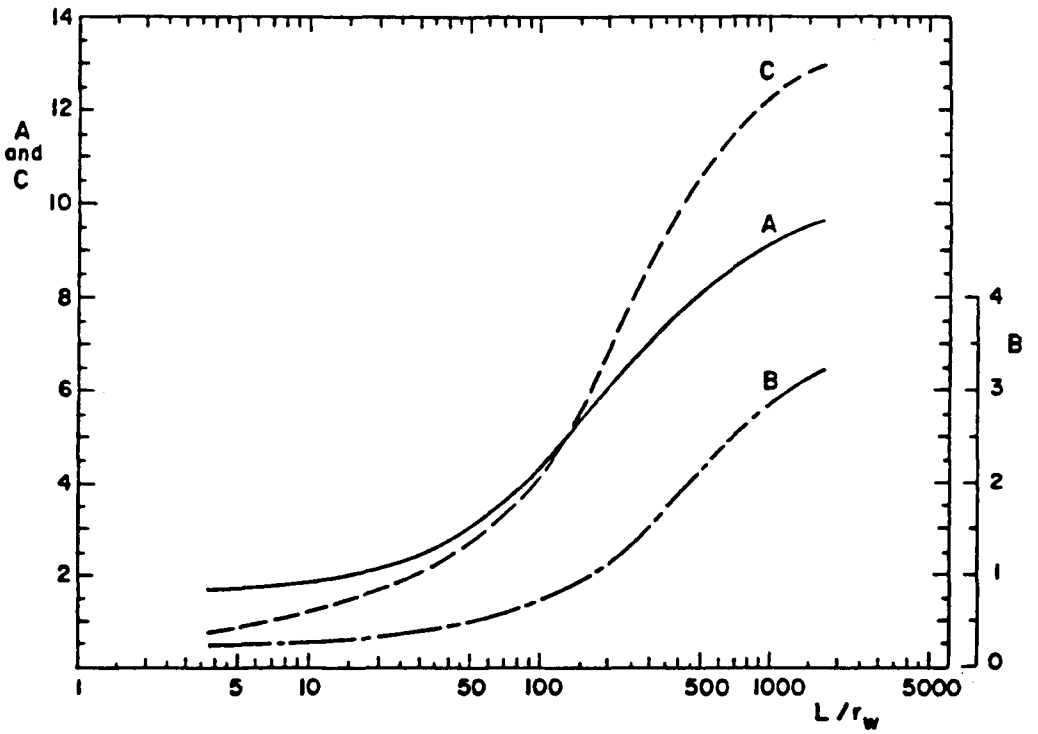


Figure 10. --Curves defining coefficients A, B, and C in equations 13 and 14 as a function of the ratio L/rw. Source: Bower and Rice, 1976.

preclude their use in problems of contaminant hydrogeology. The following references give excellent discussions of the design and interpretation of these tests: Lohman (1972), Stallman (1971), and Walton (1970).

3.6 Estimates of hydraulic conductivity for coarse-grained materials: The characterization of ground water flow systems to satisfy the intent of Part 264 Subpart F is preferably done with flow nets based on borehole measurements rather than relying on interpolation from grain-size analyses.

An empirical approach that has been used by the U.S. Geological Survey (Lappala, 1978) in several studies relates conductivity determined by aquifer testing to grain-size, degree of sorting and silt content. Table C provides the estimates of hydraulic conductivity.

Although estimates of K from analysis of grain-size and degree of sorting do provide a rough check on test values of K, repeated slug tests provide a better check on the accuracy of results.

3.7 Consolidation tests: As originally defined by Terzagi (Terzaghi and Peck, 1967) the coefficient of consolidation (C_v) of a saturated, compressible, porous medium is related to the hydraulic conductivity by:

$$C_v = \frac{K}{\rho g \alpha} \tag{15}$$

where:

K is the hydraulic conductivity, LT^{-};

ρ is the fluid density, ML^{-3};

g is the gravitational constant, LT^{-2}; and

α is the soil's compressibility, $LM^{-1}T^{2}$.

The compressibility can be determined in the laboratory with several types of consolidometers, and is a function of the applied stress and the previous loading history. Lambe (1951) describes the testing procedure.

3.7.1 The transfer value of results from this testing procedure is influenced by the extent to which the laboratory loading simulates field conditions and by the consolidation rate. The laboratory loadings will probably be less than the stress that remolded clay liner will experience; therefore, the use of an already remolded sample in the consolidometer will probably produce no measurable results. This suggests that the test is of little utility in determining the hydraulic conductivity of remolded or compacted, fine-grained soils. Second, the consolidation rate determines the length of the testing period. For granular soils, this rate is fairly rapid. For fine-grained soils, the rate may be sufficiently slow that the previously described methods,

which give faster results, will be preferable. Cohesive soils (clays) must be trimmed from undisturbed samples to fit the mold, while cohesionless sands can be tested using disturbed, repacked samples (Freeze and Cherry, 1979).

3.7.2 In general, EPA believes that consolidation tests can provide useful information for some situations, but prefers the previously described methods because they are direct measurements of hydraulic conductivity. Hydraulic conductivity values determined using consolidation tests are **not to be used** in permit applications.

3.8 Fractured media: Determining the hydraulic properties of fractured media is always a difficult process. Unlike the case with porous media, Darcy's Law is not strictly applicable to flow through fractures, although it often can be applied empirically to large bodies of fractured rock that incorporate many fractures. Describing local flow conditions in fractured rock often poses considerable difficulty. Sowers (1981) discusses determinations of hydraulic conductivity of rock. This reference should be consulted for guidance in analyzing flow through fractured media.

3.8.1 Fine-grained sediments, such as glacial tills, are commonly fractured in both saturated and unsaturated settings. These fractures may be sufficiently interconnected to have a significant influence on ground water flow, or they may be of very limited connection and be of little practical significance.

3.8.2 Frequently, a laboratory test of a small sample of clay will determine hydraulic conductivity to be on the order of 10^{-8} cm/sec. A piezometer test of the same geologic unit over an interval containing fractures may determine a hydraulic conductivity on the order of perhaps 10-5 or 10-6 cm/sec. To assess the extent of fracture interconnection, and hence the overall hydraulic conductivity of the unit, several procedures can be used. Closely spaced piezometers can be installed; one can be used as an observation well while water is added to or withdrawn from the other. Alternately, a tracer might be added to one piezometer, and the second could be monitored. These and other techniques are discussed by Sowers (1981).

3.8.3 For situations that may involve flow through fractured media, it is important to note in permit applications that an apparent hydraulic conductivity determined by tests on wells that intersect a small number of fractures may be several orders others of magnitude lower or higher than the value required to describe flow through parts of the ground water system that involve different fractures and different stress conditions from those used during the test.

4.0 CONCLUSION

4.1 By following laboratory and field methods discussed or referenced in this report, the user should be able to determine the fluid conductivity of materials used for liners, caps, and drains at waste-disposal facilities, as

well as materials composing the local ground water flow system. If fluid-conductivity tests are conducted and interpreted properly, the results obtained should provide the level of information necessary to satisfy applicable requirements under Part 264.

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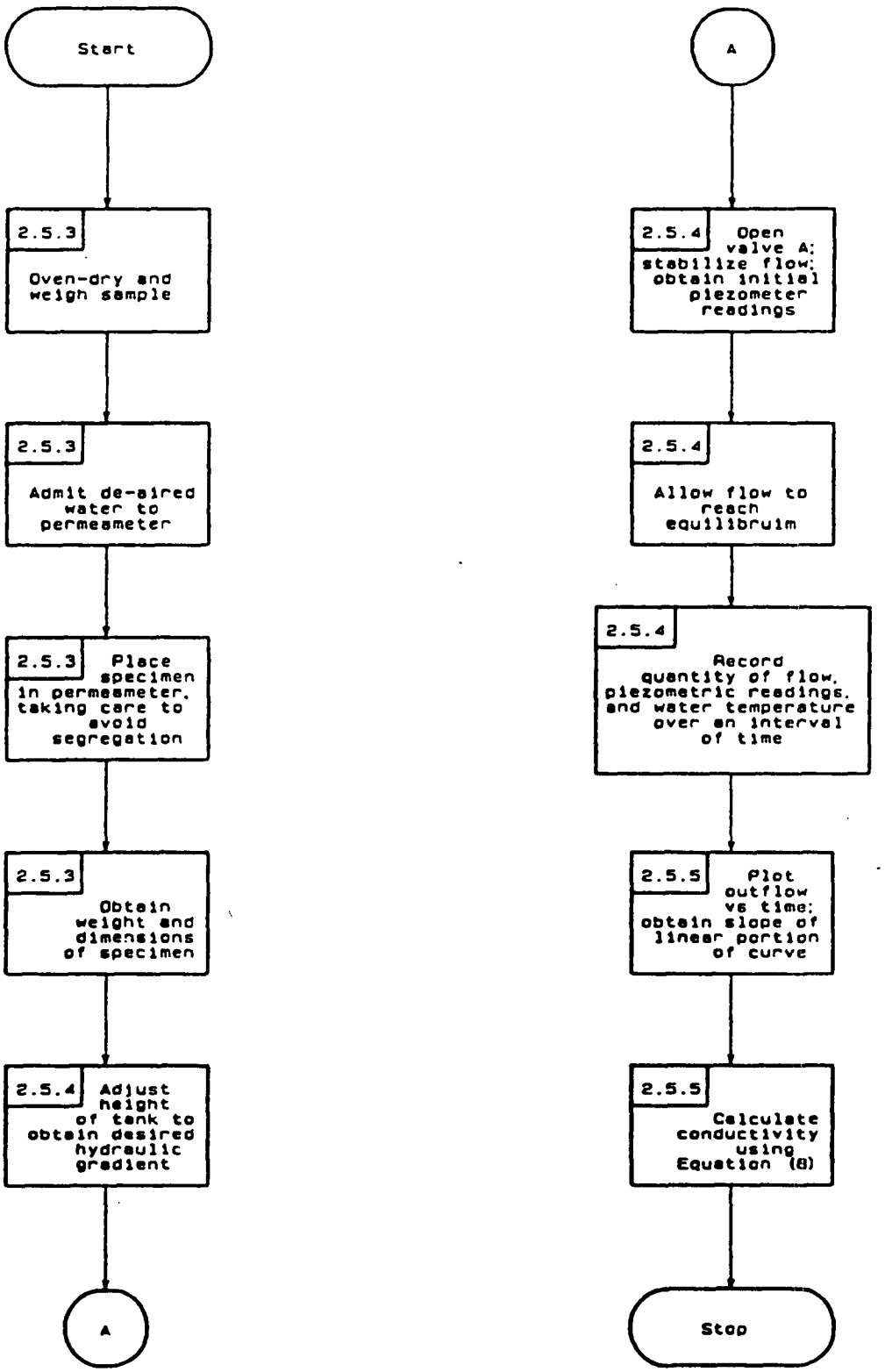
METHOD 9100 (Part)

HYDRAULIC COONDUCTIVITY OF SOIL SAMPLES:

CONSTANT-HEAD TEST WITH CONVENTIONAL PERMEAMETER



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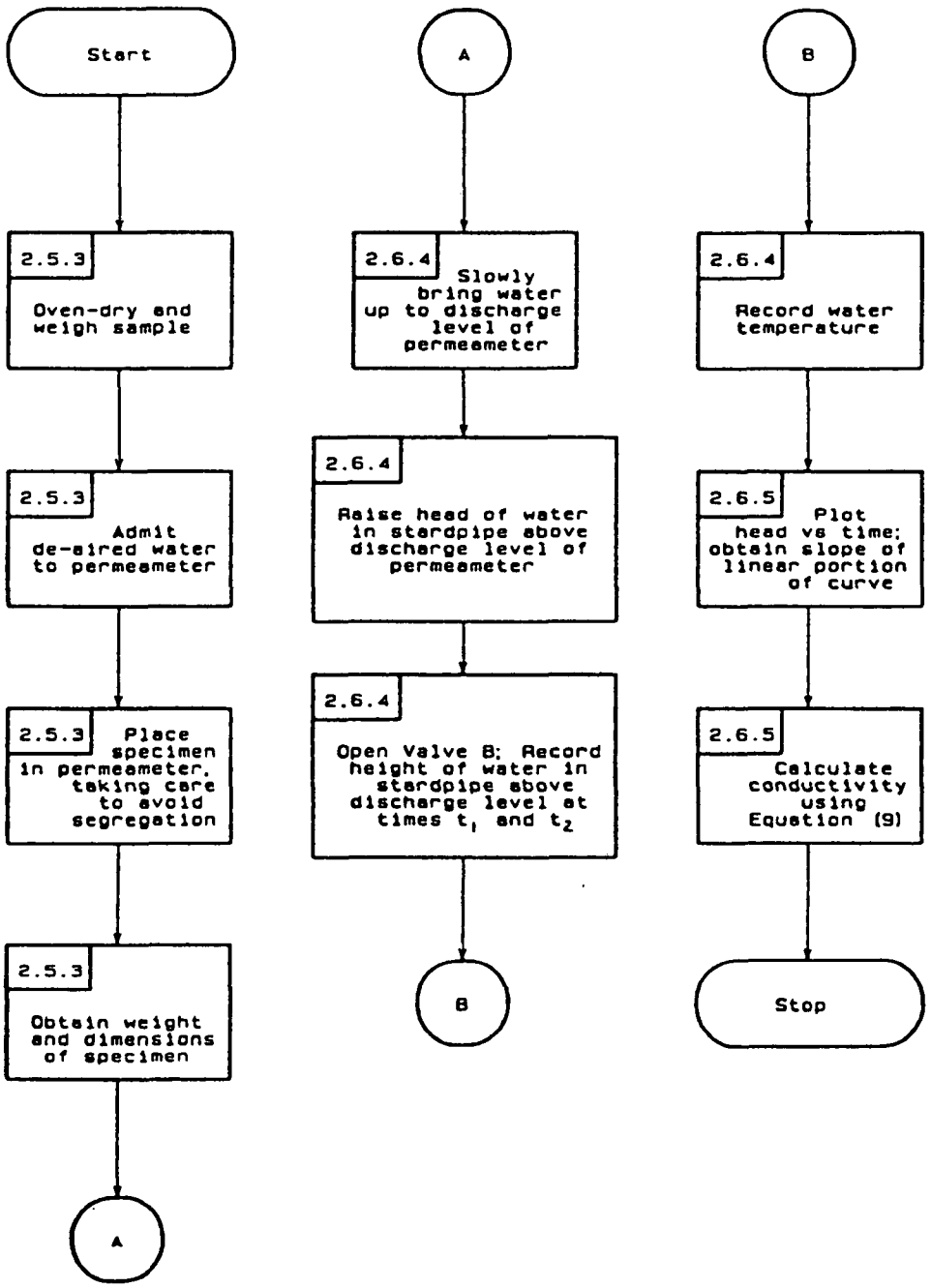
Date September 1986

METHOD 9100

HYDRAULIC CONDUCTIVITY OF SOIL SAMPLES:

FALLING-HEAD TEST WITH CONVENTIONAL PERMEAMETER



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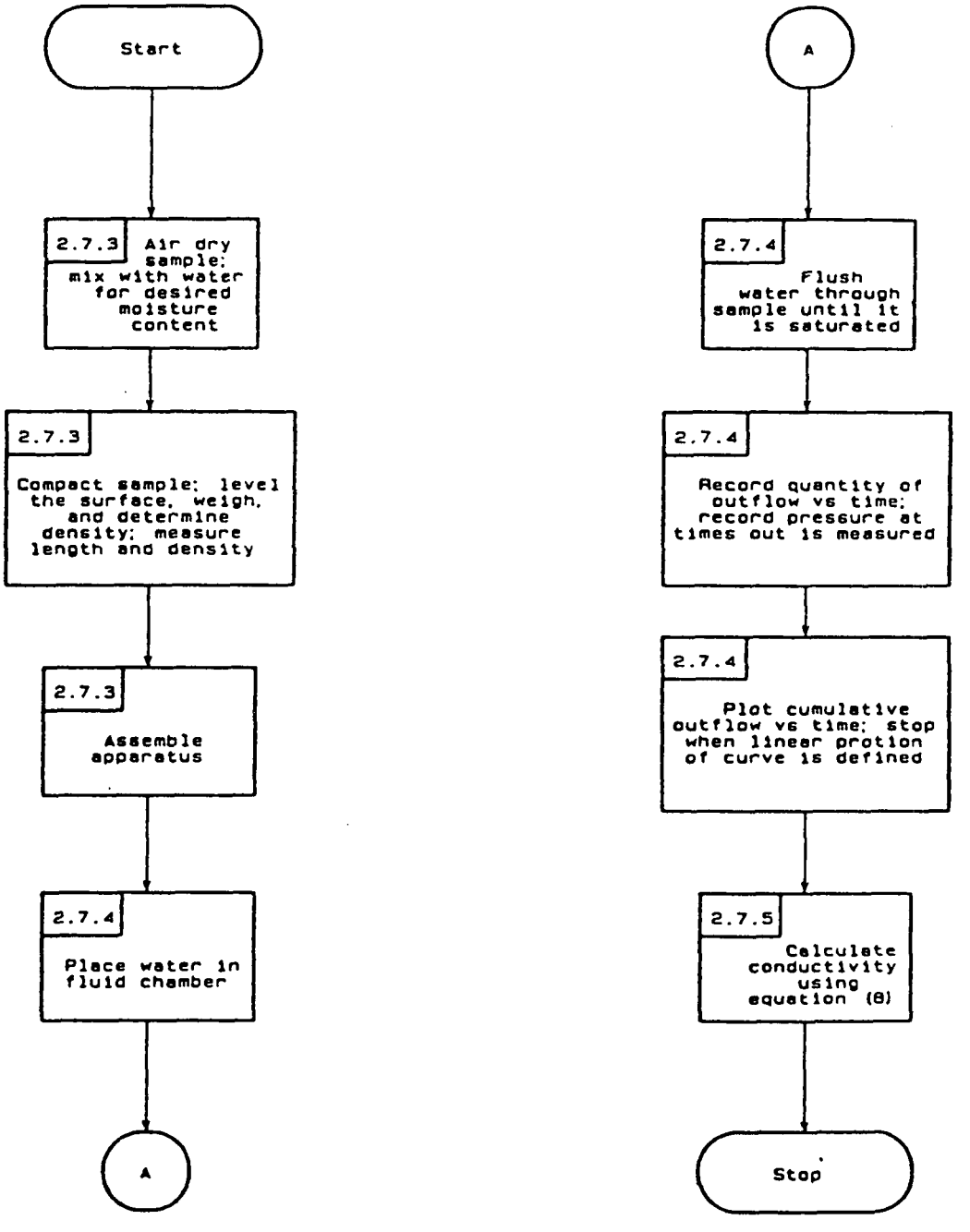
METHOD 9100

HYDRAULIC CONDUCTIVITY OF SOIL SAMPLES:

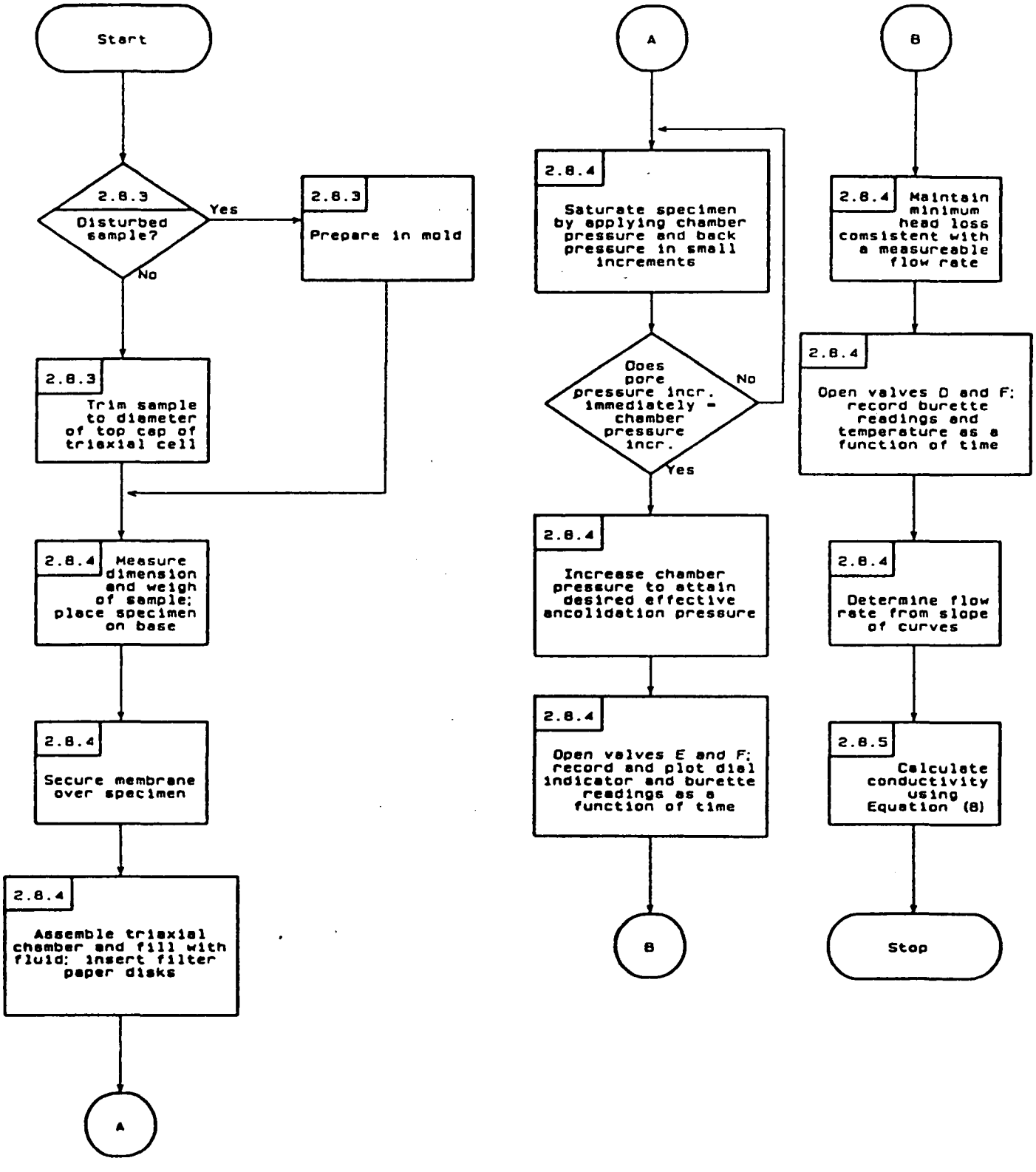
MODIFIED COMPACTION PARAMETER METHOD



METHOD 9100

HYDRAULIC CONDUCTIVITY OF SOIL SAMPLES:

TRIAXIAL CELL METHOD WITH BACK PRESSURE



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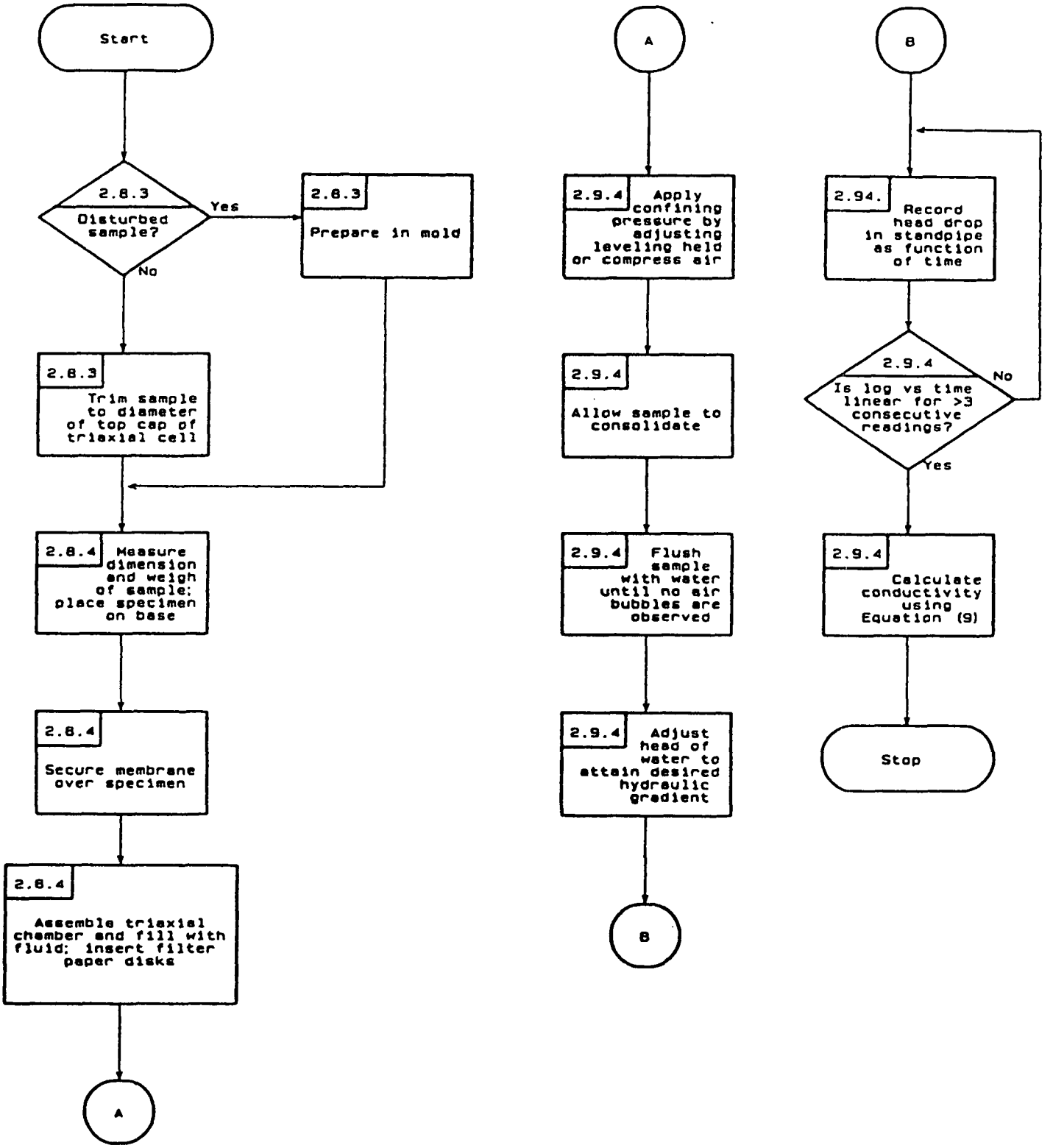
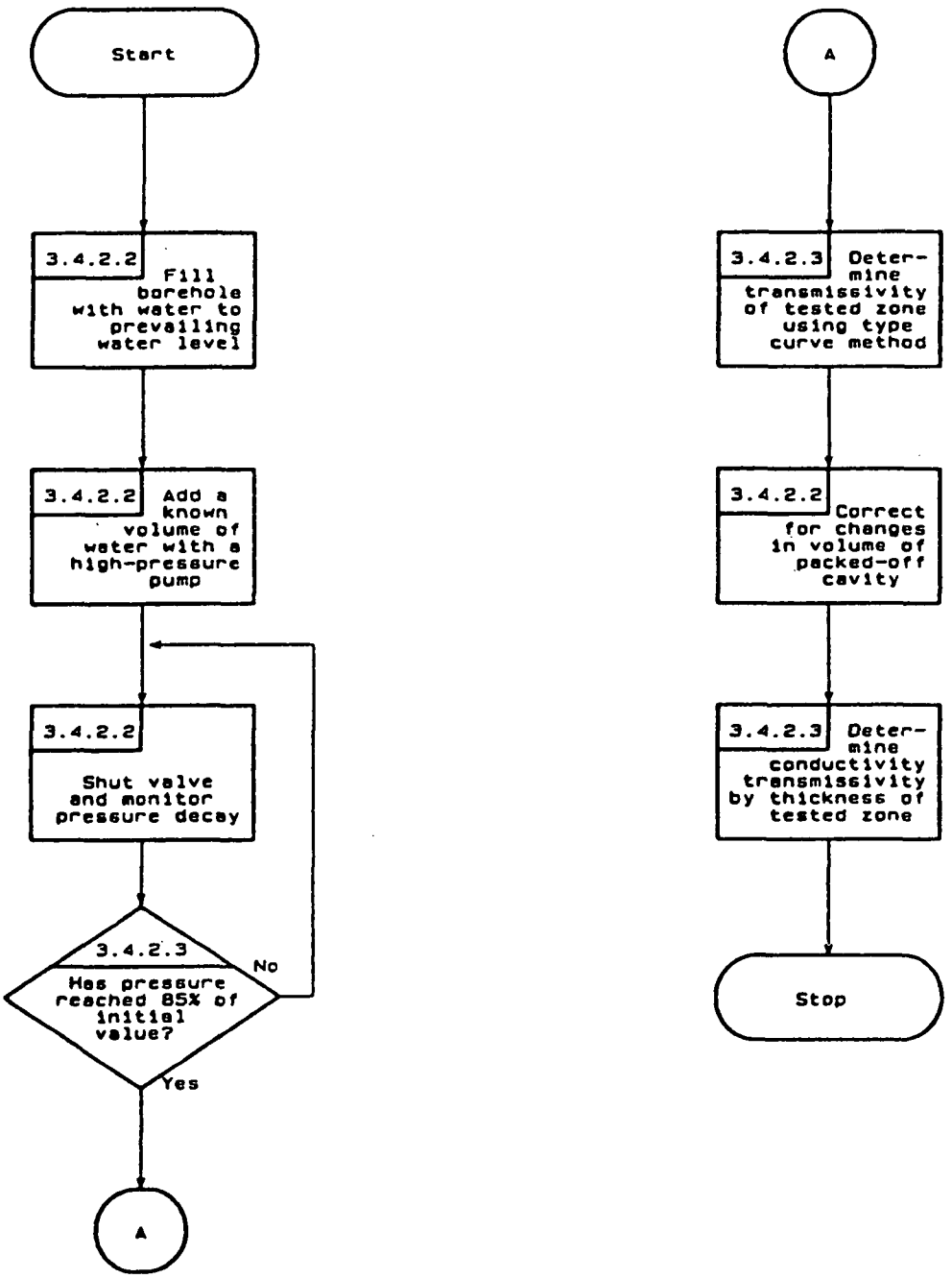

Start
2.8.3
Disturbed sample?
Yes
No
2.8.3
Prepare in mold
2.8.3
Trim sample to diameter of top cap of triaxial cell
2.8.4
Measure dimension and weigh of sample; place specimen on base
2.8.4
Secure membrane over specimen
2.8.4
Assemble triaxial chamber and fill with fluid; insert filter paper disks
A
A
2.9.4
Apply confining pressure by adjusting leveling held or compress air
2.9.4
Allow sample to consolidate
2.9.4
Flush sample with water until no air bubbles are observed
2.9.4
Adjust head of water to attain desired hydraulic gradient
B
B
2.94.
Record head drop in standpipe as function of time
2.9.4
Is log vs time linear for >3 consecutive readings?
No
Yes
2.9.4
Calculate conductivity using Equation (9)
Stop

METHOD 9100

HYDRAULIC CONDUCTIVITY OF SOIL SAMPLES:

FIELD METHODS FOR EXTREMELY TIGHT FORMATIONS UNDER CONFINED CONDITIONS



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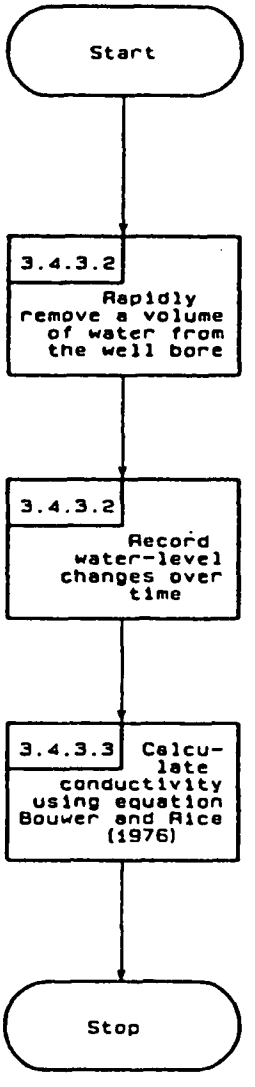
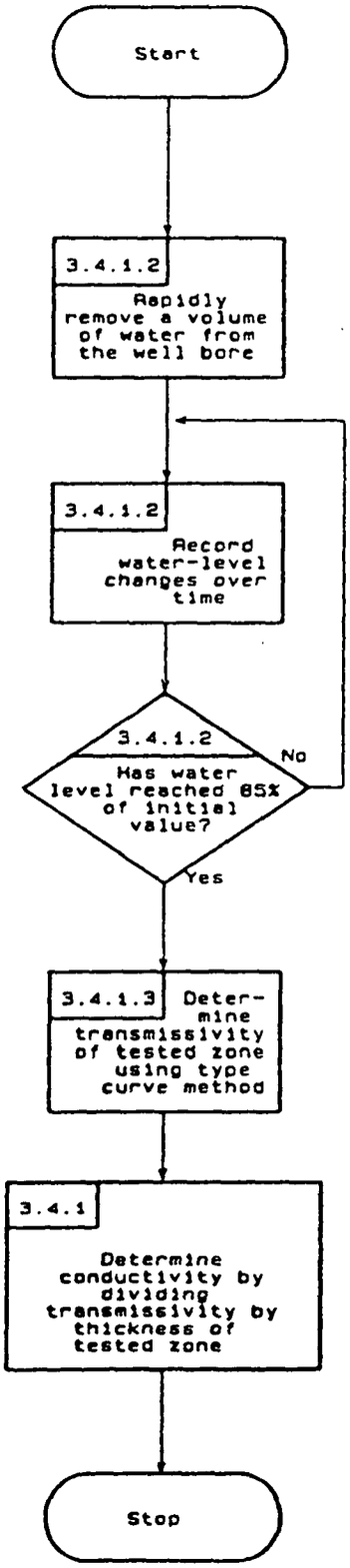
METHOD 9100

HYRAULIC CONDUCTIVITY OF SOIL SAMPLES

FIELD METHODS FOR MODERATELY PERMEABLE MATERIALS UNDER UNCONFINED CONDITIONS




Start
3.4.1.2
Rapidly remove a volume of water from the well bore
3.4.1.2
Record water-level changes over time
3.4.1.2
Has water level reached 85% of initial value?
No
Yes
3.4.1.3
Deter-mine transmissivity of tested zone using type curve method
3.4.1
Determine conductivity by dividing transmissivity by thickness of tested zone
Stop

METHOD 9310

GROSS ALPHA AND GROSS BETA

1.0 SCOPE AND APPLICATION

1.1 This method covers the measurement of gross alpha and gross beta particle activities in surface and ground waters.

1.2 The method is applicable to the measurement of alpha emitters having energies above 3.9 mega electron volts (MeV) and beta emitters having maximum energies above 0.1 MeV.

1.3 The minimum limit of concentration to which this method is applicable depends on sample size, counting-system characteristics, background, and counting time.

1.4 Because, in this method for gross alpha and gross beta measurement, the radioactivity of the sample is not separated from the solids of the sample, the solids concentration is very much a limiting factor in the sensitivity of the method for any given water sample. Also, for samples with very low concentrations of radioactivity, it is essential to analyze as large a sample aliquot as is needed to give reasonable times.

1.5 The largest sample aliquot that should be counted for gross alpha activity is that size aliquot which gives a solids density thickness of 5 mg/cm^2 in the counting planchet. For a 2-in. diameter counting planchet (20 cm^2), an aliquot containing 100 mg of nitrated dissolved solids would be the maximum aliquot size for that sample which should be evaporated and counted for gross alpha activity.

1.6 When the concentration of total solids (TS) is known for a given water sample and the alpha background and the counting efficiency of a given counting system are known, the counting time that is needed to meet the required sensitivity (3 pCi/L) can be determined by equations given in Appendix C.

1.7 For the counting of gross beta activity in a water sample, the TS is not as limiting as for gross alpha activity because beta particles are not stopped in solids as easily as are alpha particles. Very often a single sample aliquot is evaporated and counted for both gross alpha and gross beta activity. In that case, the sample aliquot size would be dictated by the solids limitations for alpha particles. For water samples that are to be counted for gross beta activity, equations in Appendix C can also be used to determine the necessary counting time to meet a sensitivity for gross beta activity (4 pCi/L).

1.8 Radionuclides that are volatile under the sample preparation conditions of this method will not be measured. In some areas of the country the nitrated water solids (sample evaporated with nitric acid present) will

not remain at a constant weight after being dried at 105°C for 2 hr and then exposed to the atmosphere before and during counting. Other radioactivities (such as some chemical forms of radioiodine) may also be lost during the sample evaporation and drying at 105°C. Those types of water samples need to be heated to a dull red heat for a few minutes to convert the salts to oxides. Sample weights are then usually sufficiently stable to give consistent counting rates, and a correct counting efficiency can then be assigned. Some radioactivities, such as the cesium radioisotopes, may be lost when samples are heated to a dull red color. Such losses are limitations of the test method.

1.9 This method provides a rapid screening measurement to indicate whether specific analyses are required. When the gross alpha particle activity exceeds 5 pCi/L, the same or an equivalent sample shall be analyzed for alpha-emitting radium isotopes (Method 9315) or an alternative measurement of radium-226 alpha emission (Standard Methods for the Examination of Water and Wastewater, 15th edition, Method 705 or 706, respectively). Gross beta particle emissions exceeding 15 pCi/L in a sample shall be analyzed for strontium-89 and cesium-134 (Standard Methods for the Examination of Water and Wastewater, 15th edition, Methods 704 and 709, respectively). If gross beta activity exceeds 50 pCi/L, the identity of the major radioactive constituents must be evaluated and the appropriate organ and total body doses determined.

2.0 SUMMARY OF METHOD

2.1 An aliquot of a preserved water sample is evaporated to a small volume and transferred quantitatively to a tared 2-in. stainless steel counting planchet. The sample residue is dried to constant weight, reweighed to determine dry residue weight, and then counted for alpha and/or beta radioactivity.

2.2 Counting efficiencies for both alpha and beta particle activities are selected according to the amount of sample solids from counting efficiency vs. sample solids standard curves.

3.0 INTERFERENCES

3.1 Moisture absorbed by the sample residue is an interference because it obstructs counting and self-absorption characteristics. If a sample is counted in an internal proportional counter, static charge on the sample residue can cause erratic counting, thereby preventing an accurate count.

3.2 Nonuniformity of the sample residue in counting planchet interferes with the accuracy and precision of the method.

3.3 Sample density on the planchet area should be not more than 10 mg/cm^2 for gross alpha and not more than 20 mg/cm^2 for gross beta.

3.4 When counting alpha and beta particle activity by a gas-flow proportional counting system, counting at the alpha plateau discriminates against beta particle activity, whereas counting at the beta plateau is sensitive to alpha particle activity present in the sample. This latter effect should be determined and compensated for during the calibration of the specific instrument being used.

4.0 APPARATUS AND MATERIALS

4.1 Gas-flow proportional counting system, or

4.2 Scintillation detection system, or

4.3 Stainless steel counting planchets.

4.4 Electric hot plate.

4.5 Drying oven.

4.6 Drying lamp.

4.7 Glass desiccator.

4.8 Glassware.

4.9 Analytical balance.

5.0 REAGENTS

5.1 All chemicals should be of "reagent-grade" or equivalent whenever they are commercially available.

5.2 Distilled or deionized water (Type II) having a resistance value between 0.5 and 2.0 megaohms (2.0 to 0.5 mhos)/cm at 25°C.

5.3 Nitric acid, 1 N: Mix 6.2 mL 16 N HNO_3 (conc.) with deionized or distilled water and dilute to 100 mL.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected in a manner which addresses the considerations discussed in Chapter Nine of this manual.

6.2 It is recommended that samples be preserved at the time of collection by adding enough 1 N HNO_3 to the sample to bring it to pH 2 (15 mL 1 N HNO_3 per liter of sample is usually sufficient). If samples are to be collected without preservation, they should be brought to the laboratory within 5 days and then preserved and held in the original container for a minimum of 16 hr before analysis or transfer of the sample.

6.3 The container choice should be plastic rather than glass to prevent loss due to breakage during transportation and handling.

7.0 PROCEDURE

7.1 Calibration:

7.1.1 For absolute gross alpha and gross beta measurement, the detectors must be calibrated to obtain the ratio of count rate to disintegration rate. Americium-241 (used for alpha activity in the collaborative test of this method) has higher alpha particle energy and radium-226 radionuclides but is close to the energy of the alpha particles emitted by naturally occurring thorium-228 and radium-224. Standards should be prepared in the geometry and weight ranges to be encountered in these gross analyses. It is, therefore, the prescribed radionuclide for gross alpha calibration. NBS or NBS-traceable americium-241 is available from Standard Reference Materials Catalog, NBS Special Publications 260, U.S. Department of Commerce (1976) and from Quality Assurance Branch, EMSL-LV, P.O. Box 15027, Las Vegas, Nevada 89114.

7.1.2 Strontium-90 and cesium-137 have both been used quite extensively as standards for gross beta activity. Standard solutions of each of these radionuclides are readily available. Cesium is volatile at elevated temperatures (above 450°C). Some water supplies have dissolved solids (salts) that, when converted to nitrate salts, are quite hygroscopic and need to be converted to oxides by heating to red heat to obtain sample aliquots that are weight-stable. Sample weight stability is essential to gross alpha and gross beta measurements to ensure the accuracy of the self-absorption counting efficiency factor to be used for the samples. Strontium-90 in equilibrium with its daughter yttrium-90 is the prescribed radionuclide for gross beta calibrations.

7.1.3 For each counting instrument to be used, the analyst should prepare separate alpha and beta particle self-absorption graphs showing water sample residue weight (mg) vs. the efficiency factor (cpm/dpm), using standard alpha and beta emitter solutions and tap water. For the alpha graph standard, alpha activity is added to varying sizes of aliquots of tap water such that the aliquot residue weight is varied between 0 and 100 mg (for a 2-in. counting planchet). A similar graph is prepared with standard beta activity and tap-water aliquots, varying the residue weight between 0 and 300 mg (for a 2-in. planchet). If it is planned to use water-sample aliquot volumes that always contain 100 mg of dried water solids, then only the efficiency factor for that residue weight needs to be established.

7.1.4 Tap water aliquots, with added americium-241 or strontium-90 standard, should be acidified with a few mL 16 N HNO_3, evaporated to a small volume in a beaker on a hot plate, transferred quantitatively in 5-mL portions or less to a tared counting planchet, evaporated to dryness, and finally dried at 105°C for 1 hr (or flamed to a red heat if dried

solids appear to be noticeably hygroscopic). Weight-stable aliquot residues should then be alpha and/or beta counted until at least 10,000 total counts have been accumulated. A single set of reference standards prepared in this way can be used for each counting instrument for separate graph preparations and can be stored for reverification whenever needed.

7.2 Transfer to a beaker an aliquot of water sample of a volume that contains no more than 100 mg (for alpha only or alpha and beta determination) or 200 mg (for beta only determination) of total water solids. Evaporate the aliquot to near dryness on a hot plate. If water samples are known or suspected to contain chloride salts, those chloride salts should be converted to nitrate salts before the sample residue is transferred to a stainless steel planchet (chlorides will attack stainless steel and increase the sample solids, and no correction can be made for those added solids). Chloride salts can be converted to nitrate salts by adding 5-mL portions of 16 N HNO_3 to the sample residue and evaporating to near dryness. (Two treatments are usually sufficient.) Add 10 mL 1 N HNO_3 to the beaker and swirl to dissolve the residue. Quantitatively transfer the aliquot concentrate in small portions (not more than 5 mL at a time) to a tared planchet, evaporating each portion to dryness.

7.3 Dry the sample residue in a drying oven at 105°C for at least 1 hr, cool in a desiccator, weigh, and count. Store the sample residue in a desiccator until ready for counting.

7.4 Some types of water-dissolved solids, when converted to nitrate salts, are quite hygroscopic even after being dried at 105°C for 1 hr. When such hygroscopic salts are present with samples that are put into an automatic counting system, those samples gain weight while they are waiting to be counted, and inaccurate counting data result. When there is evidence of hygroscopic salts in sample counting planchets, it is recommended that they be flamed to a dull red heat with a Meeker burner for a few minutes to convert the nitrate salts to oxides before weighing and counting. (It is possible to have a loss of cesium during the flaming of the samples.)

7.5 Count for alpha and beta activity at their respective voltage plateaus. If the sample is to be recounted for reverification, store it in a desiccator.

NOTE: As long as counting chambers are capable of handling the same size planchet, alpha and beta activities can be determined at their respective voltage plateaus in the designated counting instruments. Keep the planchet in the desiccator until ready to count because vapors from moist residue can damage detector and window and can cause erratic measurements. If the gas-flow internal proportional counter does not discriminate for the higher energy alpha pulses at the beta plateau, the alpha activity must be subtracted from the beta plus alpha activity. This is particularly important for samples with high alpha activity.

7.6 Calculations:

7.6.1 Calculate the alpha radioactivity by the following equation:

$$\text{Alpha (pCi/liter)} = \frac{A \times 1{,}000}{2.22 \times C \times V}$$

where:

A = net alpha count rate (gross alpha count rate minus the background count rate) at the alpha voltage plateau;

C = alpha efficiency factor, read from the graph (Paragraph 7.1.3) of efficiency vs. mg of water solids per cm^2 of planchet area, cpm/dpm);

V = volume of sample aliquot (mL); and

2.22 = conversion factor from dpm/pCi.

7.6.2 Calculate the beta radioactivity by the following equations:

7.6.2.1 If there are no significant alpha counts when the sample is counted at the alpha voltage plateau, the beta activity can be determined from the following equation:

$$\text{Beta (pCi/liter)} = \frac{B \times 1{,}000}{2.22 \times D \times V}$$

where:

B = net beta count rate (gross alpha count rate minus the background count rate at the beta voltage plateau),

D = beta efficiency factor, read from the graph (Paragraph 7.1.3) of efficiency vs. mg of water solids per cm^2 of planchet area, (cpm/dpm).

V = volume of sample aliquot (mL).

2.22 = conversion factor from dpm/pCi.

7.6.3 When counting beta radioactivity in the presence of alpha radioactivity by gas-flow proportional counting systems (at the beta plateau), alpha particles are also counted. Because alpha particles are more readily absorbed by increasing sample thickness than beta particles, the alpha/beta count ratios vary with increasing sample thickness. Therefore, it is necessary to prepare a calibration curve by counting standards containing americium-241 with increasing thickness of solids on

the alpha plateau and then on the beta plateau, plotting the ratios of the two counts vs. density thickness. The alpha amplification factor (E) from that curve is used to correct the amplified alpha count on the beta plateau. When significant alpha activity is indicated by the sample count at the alpha voltage plateau, the beta activity of the sample can be determined by counting the sample at the beta voltage plateau and calculating the activity from the following equation:

$$\text{Beta (pCi/liter)} = \frac{(B - AE) \times 1{,}000}{2.22 \times D \times V}$$

where:

B = as defined above.

D = as defined above.

A = as defined above.

E = alpha amplification factor, read from the graph of the ratio of alpha counted at the beta voltage/alpha counted at the alpha voltage vs. sample density thickness.

V = volume of sample aliquot (mL).

2.22 = conversion factor from dpm/pCi.

7.7 Errors associated with the results of the analysis should also be reported.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination is occurring.

8.3 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample-preparation and analytical process.

8.4 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

9.0 METHOD PERFORMANCE

9.1 In a collaborative study of two sets of paired water samples containing known additions of radionuclides, 15 laboratories determined the gross alpha activity and 16 analyzed gross beta activity. The samples contained simulated water minerals of approximately 350 mg fixed solids/L. The alpha results of one laboratory were rejected as outliers.

The average recoveries of added gross alpha activity were 86, 87, 84, and 82%. The precision (random error) at the 95% confidence level was 20 and 24% for the two sets of paired samples. The method was biased low, but not seriously.

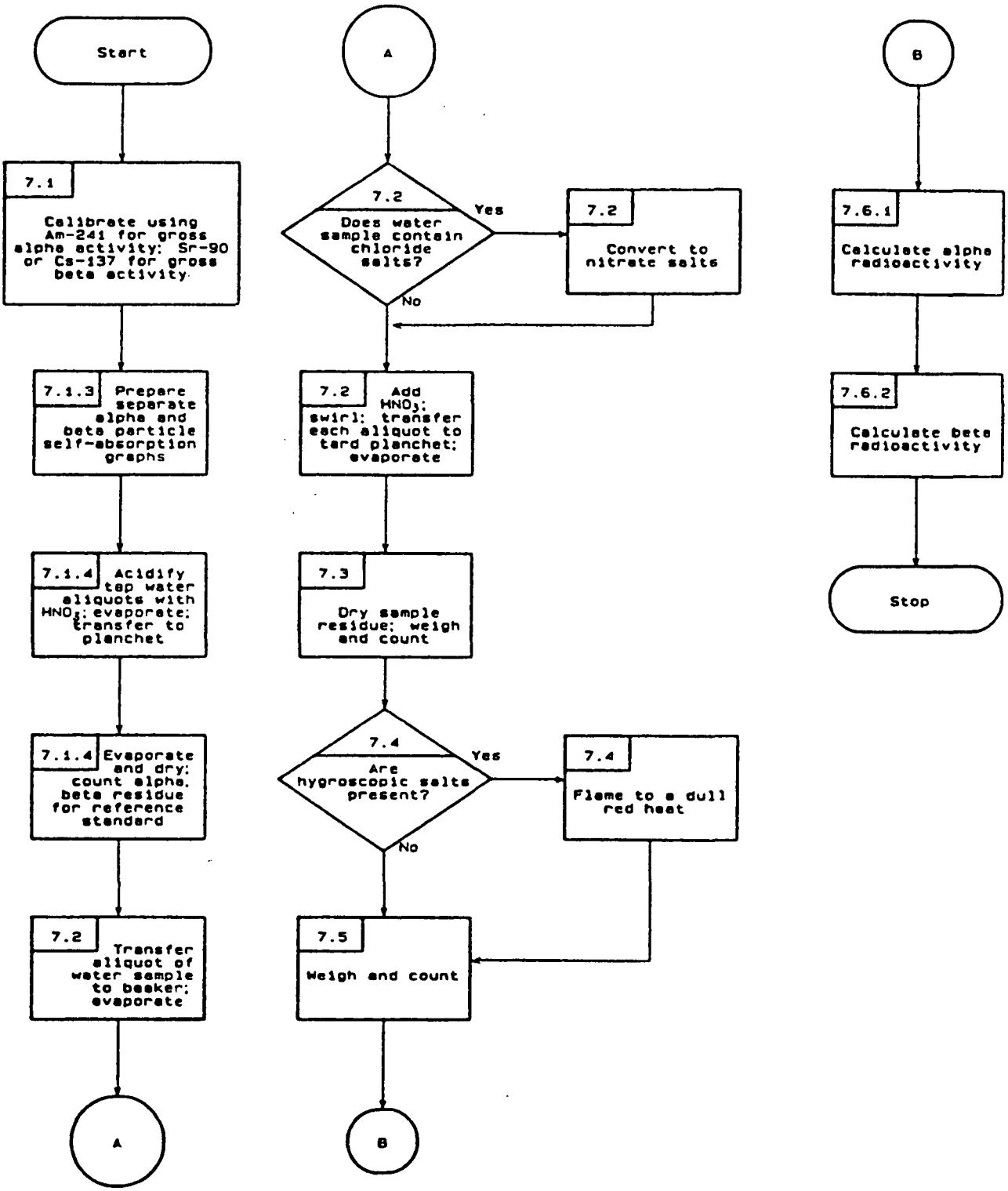
The average recoveries of added gross beta activity were 99, 100, 100, and 100%. The precision (random error) at the 95% confidence level was 12 and 18% for the two sets of paired samples. The method showed no bias.

10.0 REFERENCES

10.1 None required.

METHOD 9310

GROSS ALPHA AND GROSS BETA



Revision 0
Date September 1986

METHOD 9315

ALPHA-EMITTING RADIUM ISOTOPES

1.0 SCOPE AND APPLICATION

1.1 This method covers the measurement of the total soluble alpha-emitting radioisotopes of radium, namely radium-223, radium-224, and radium-226, in surface and ground waters.

1.2 Although the method does not always give an accurate measurement of the radium-226 content of the sample (when other radium alpha emitters are present), it can be used to screen samples. When the total radium alpha activity of a drinking water sample is greater than 5 pCi/L, then the radium-226 analysis is required. If the level of radium-226 exceeds 3 pCi/L, the sample must also be measured for radium-228 (Method 9320).

1.3 Because this method provides for the separation of radium from other water-dissolved solids in the sample, the sensitivity of the method is a function of sample size, reagent and instrument background, counting efficiency, and counting time.

1.4 Absolute measurement can be made by calibrating the alpha detector with standard radium-226 in the geometry obtained with the final precipitate.

2.0 SUMMARY OF METHOD

2.1 The radium in the surface water or ground water sample is collected by coprecipitation with barium and lead sulfate and purified by reprecipitation from EDTA solution. Citric acid is added to the water sample to assure that complete interchange occurs before the first precipitation step. The final $BaSO_4$ precipitate, which includes radium-226, radium-224, and radium-223, is alpha counted to determine the total disintegration rate of the radium isotopes.

2.2 The radium activities are counted in an alpha counter where efficiency for determining radium-226 has been calibrated with a standard of known radium-226 activity. By making a correction for the ingrowth of alpha activity in radium-226 for the elapsed time after separation, one can determine radium activity in the sample. Because some daughter ingrowth can occur before the separated radium is counted, it is necessary to make activity corrections for the count rate. A table of ingrowth factors for various times after radium separation is provided in Paragraph 7.14.

3.0 INTERFERENCES

3.1 Inasmuch as the radiochemical yield of the radium activity is based on the chemical yield of the $BaSO_4$ precipitate, the presence of significant natural barium in the sample will result in a falsely high chemical yield.

3.2 Radium isotopes are separated from other alpha-emitting radionuclides by this method.

3.3 The alpha count of the separated radium must be corrected for its partially ingrown alpha-emitting daughters.

4.0 APPARATUS AND MATERIALS

4.1 Alpha scintillation or a gas-flow proportional alpha particle counting system with low background (<1 cpm).

4.2 Stainless steel counting planchets.

4.3 Electric hot plate.

4.4 Drying oven and/or drying lamp.

4.5 Glass desiccator.

4.6 Analytical balance.

4.7 Centrifuge.

4.8 Glassware.

5.0 REAGENTS

5.1 Distilled or deionized water (Type II).

5.2 Acetic acid, 17.4 N: glacial CH_3COOH (conc.), sp. gr. 1.05, 99.8%.

5.3 Ammonium sulfate, 200 mg/mL: Dissolve 20 g $(NH_4)_2SO_4$ in a minimum of water and dilute to 100 mL.

5.4 Barium carrier, 16 mg/mL, standardized:

5.4.1 Dissolve 2.846 g $BaCl_2 \cdot 2H_2O$ in water, add 0.5 mL 16 N HNO_3, and dilute to 100 mL with water.

5.4.2 To perform standardization (in triplicate): Pipette 2.0 mL carrier solution into a centrifuge tube containing 15 mL water. Add 1 mL 18 N H_2SO_4 with stirring and digest precipitate in a water bath for 10 min. Cool, centrifuge, and decant the supernatant. Wash precipitate with 15 mL water. Transfer the precipitate to a tared stainless steel planchet with a minimum of water. Dry under infrared lamp, store in desiccator, and weigh as $BaSO_4$.

5.5 Citric acid, 1 M: Dissolve 19.2 g $C_6H_8O_7 \cdot H_2O$ in water and dilute to 100 mL.

5.6 EDTA reagent, basic (0.25 M): Dissolve 20 g NaOH in 750 mL water, heat and slowly add 93 g disodium ethylenedinitriloacetate dihydrate ($Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$). Heat and stir until dissolved; filter through coarse filter paper and dilute to 1 liter.

5.7 Lead carrier, 15 mg/mL: Dissolve 2.397 g $Pb(NO_3)_2$ in water, add 0.5 mL 16 N HNO_3, and dilute to 100 mL with water.

5.8 Sodium hydroxide, 6 N: Dissolve 24 g NaOH in 80 mL water and dilute to 100 mL.

5.9 Sulfuric acid, 18 N: Cautiously mix 1 volume 36 N H_2SO_4 (concentrated) with 1 volume of water.

5.10 Sulfuric acid, 0.1 N: Mix 1 volume 18 N H_2SO_4 with 179 volumes of water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected in a manner which addresses the considerations discussed in Chapter Nine of this manual.

6.2 It is recommended that samples be preserved at the time of collection by adding enough 1 N HNO_3 to the sample to bring it to pH 2 (15 mL 1 N HNO_3 per liter of sample is usually sufficient). If samples are to be collected without preservation, they should be brought to the laboratory within 5 days and then preserved and held in the original container for a minimum of 16 hr before analysis or transfer of the sample.

6.3 The container choice should be plastic rather than glass to prevent loss due to breakage during transportation and handling.

7.0 PROCEDURE

7.1 Calibration:

7.1.1 The counting efficiency for radium alpha particles with barium sulfate carrier present must be determined using a standard (known) radium alpha activity and 32 mg of barium carrier as $BaSO_4$ (same carrier amount used in samples). This is done with spiked distilled water samples, and the procedure for regular samples is followed. Note the time of the Ra-$BaSO_4$ precipitation.

7.1.2 The radium alpha counting efficiency, E, is calculated as follows:

$$E\ (cpm/dpm) = \frac{C}{A \times I}$$

where:

C = sample net cpm (gross counts minus background divided by the counting time in minutes).

A = dpm of radium-226 added to sample.

I = ingrowth factor for the elapsed time from Ra-$BaSO_4$, precipitation to midpoint of counting time.

7.2 To a 1,000-mL surface water or ground water sample, add 5 mL 1 M $C_6H_8O_7 \cdot H_2O$, 1 mL lead carrier, and 2.0 mL barium carrier, and heat to boiling.

7.3 Cautiously, with vigorous stirring, add 20 mL 18 N H_2SO_4. Digest 5 to 10 min and let the mixed $BaSO_4$-$PbSO_4$ precipitate settle overnight. Decant and discard supernate.

7.4 Transfer the precipitate to a centrifuge tube with a minimum amount of 0.1 N H_2SO_4. Centrifuge and discard supernate.

7.5 Wash the precipitate twice with 0.1 N H_2SO_4. Centrifuge and discard washes.

7.6 Dissolve the precipitate by adding 15 mL basic EDTA reagent; heat in a hot-water bath and add a few drops 6 N NaOH until solution is complete.

7.7 Add 1 mL $(NH_4)_2SO_4$ (200 mg/mL) and stir thoroughly. Add 17.4 N CH_3COOH dropwise until precipitation begins and then add 2 mL extra. Digest 5 to 10 min.

7.8 Centrifuge, discard the supernate, and record time.
NOTE: At this point, the separation of the $BaSO_4$ is complete, and the ingrowth of radon (and daughters) commences.

7.9 Wash the $BaSO_4$ precipitate with 15 mL water, centrifuge, and discard wash.

7.10 Transfer the precipitate to a tared stainless steel planchet with a minimum of water and dry under infrared lamps.
NOTE: Drying should be rapid, but not too vigorous, to minimize any loss of radon-222 that has already grown into the precipitate.

7.11 Cool, weigh, and store in desiccator.

7.12 Count in a gas-flow internal proportional counter or an alpha scintillation counter to determine the alpha activity.

7.13 Calculation:

7.13.1 Calculate the radium-226 concentration, D (which would include any radium-224 and radium-223 that is present), in picocuries per liter as follows:

$$D = \frac{C}{2.22 \times E \times V \times R \times I}$$

where:

C = net count rate, cpm.

E = counter efficiency, for radium-226 in $BaSO_4$ predetermined for this procedure (see Paragraph 7.1.2).

V = liters of sample used.

R = fractional chemical yield.

I = ingrowth correction factor (see Paragraph 7.14).

2.22 = conversion factor from dpm/pCi.

7.14 It is not always possible to count the $BaSO_4$ precipitate immediately after separation; therefore, corrections must be made for the ingrowth of the radium-226 daughters between the time of separation and counting, according to the following table:

Hours from separation to counting	Ingrowth correction factor
0	1.00
1	1.02
2	1.04
3	1.06
4	1.08
5	1.10
6	1.12
24	1.49
48	1.91
72	2.25
96	2.54
120	2.78
144	2.99
192	3.29
240	3.51

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample-preparation process.

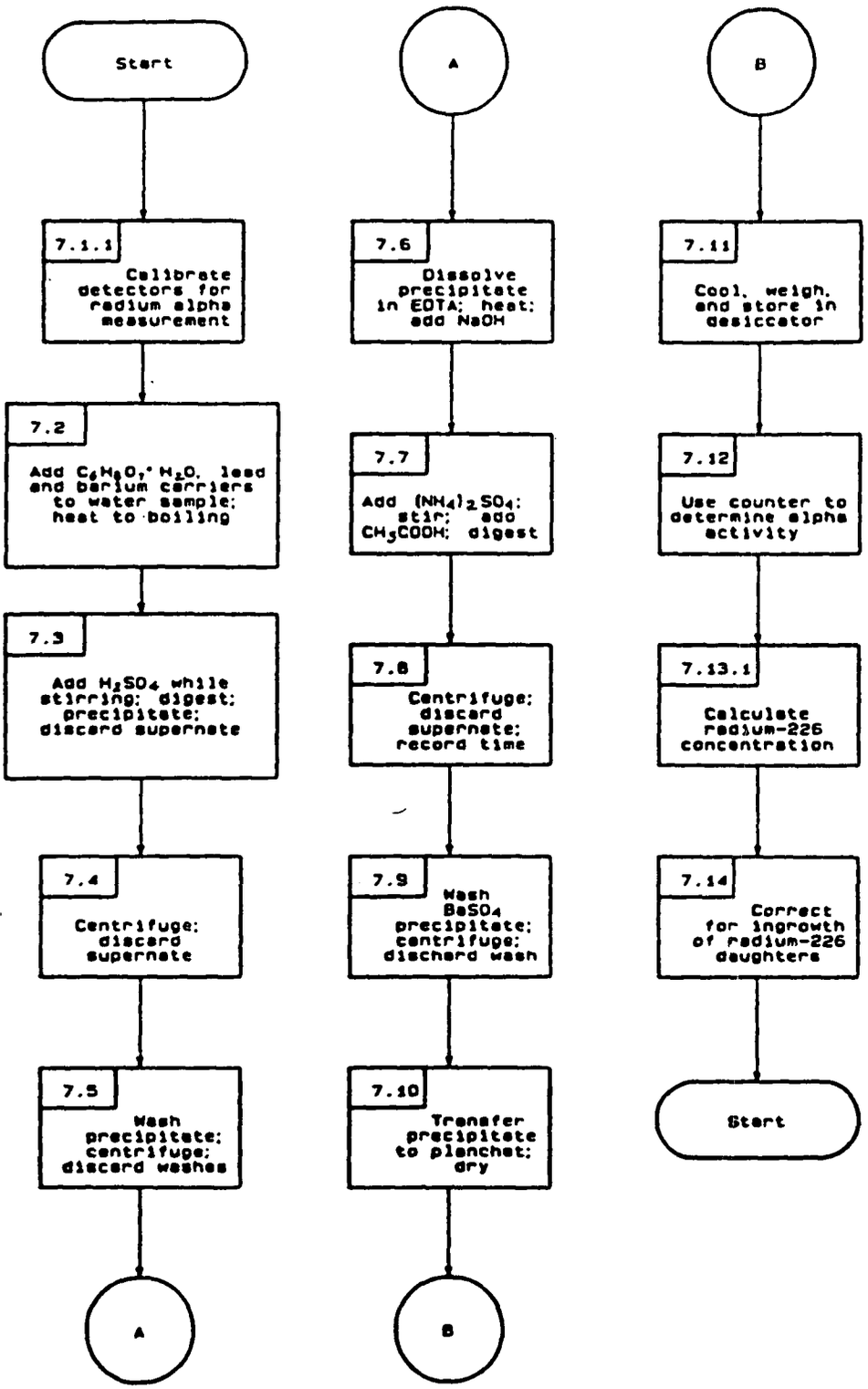
8.4 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

10.1 None required.


Start
7.1.1
Calibrate detectors for radium alpha measurement
7.2
Add $C_6H_8O_7 \cdot H_2O$, lead and barium carriers to water sample; heat to boiling
7.3
Add H_2SO_4 while stirring; digest; precipitate; discard supernate
7.4
Centrifuge; discard supernate
7.5
Wash precipitate; centrifuge; discard washes
A
A
7.6
Dissolve precipitate in EDTA; heat; add NaOH
7.7
Add $(NH_4)_2SO_4$; stir; add CH_3COOH; digest
7.8
Centrifuge; discard supernate; record time
7.9
Wash $BaSO_4$ precipitate; centrifuge; discard wash
7.10
Transfer precipitate to planchet; dry
B
B
7.11
Cool, weigh, and store in desiccator
7.12
Use counter to determine alpha activity
7.13.1
Calculate radium-226 concentration
7.14
Correct for ingrowth of radium-226 daughters
Start

PART II CHARACTERISTICS

CHAPTER SEVEN

INTRODUCTION AND REGULATORY DEFINITIONS

7.1 IGNITABILITY

7.1.1 Introduction

This section discusses the hazardous characteristic of ignitability. The regulatory background of this characteristic is summarized, and the regulatory definition of ignitability is presented. The two testing methods associated with this characteristic, Methods 1010 and 1020, can be found in Chapter Eight.

The objective of the ignitability characteristic is to identify wastes that either present fire hazards under routine storage, disposal, and transportation or are capable of severely exacerbating a fire once started.

7.1.2 Regulatory Definition

The following definitions have been taken nearly verbatim from the RCRA regulations (40 CFR 261.21) and the DOT regulations (49 CFR §§ 173.300 and 173.151).

Characteristics Of Ignitability Regulation

A solid waste exhibits the characteristic of ignitability if a representative sample of the waste has any of the following properties:

1. It is a liquid, other than an aqueous solution, containing < 24% alcohol by volume, and it has a flash point < 60°C (140°F), as determined by a Pensky-Martens Closed Cup Tester, using the test method specified in ASTM Standard D-93-79 or D-93-80, or a Setaflash Closed Cup Tester, using the test method specified in ASTM standard D-3278-78, or as determined by an equivalent test method approved by the Administrator under the procedures set forth in Sections 260.20 and 260.21. (ASTM standards are available from ASTM, 1916 Race Street, Philadelphia, PA 19103.)

2. It is not a liquid and is capable, under standard temperature and pressure, of causing fire through friction, absorption of moisture, or spontaneous chemical changes and, when ignited, burns so vigorously and persistently that it creates a hazard.

3. It is an ignitable compressed gas, as defined in 49 CFR 173.300 and as determined by the test methods described in that regulation or by equivalent test methods approved by the Administrator under Sections 260.20 and 260.21.

4. It is an oxidizer, as defined in 49 CFR 173.151.

Ignitable Compressed Gas

For the purpose of this regulation the following terminology is defined:

1. Compressed gas. The term "compressed gas" shall designate any material or mixture having in the container an absolute pressure exceeding 40 psi at 21°C (70°F) or, regardless of the pressure at 21°C (70°F), having an absolute pressure exceeding 104 psi at 54°C (130°F), or any liquid flammable material having a vapor pressure exceeding 40 psi absolute at 38°C (100°F), as determined by ASTM Test D-323.

2. Ignitable compressed gas. Any compressed gas, as defined in Paragraph 1, above, shall be classed as an "ignitable compressed gas" if any one of the following occurs:

   a. Either a mixture of 13% or less (by volume) with air forms a flammable mixture, or the flammable range with air is wider than 12%, regardless of the lower limit. These limits shall be determined at atmospheric temperature and pressure. The method of sampling and test procedure shall be acceptable to the Bureau of Explosives.

   b. Using the Bureau of Explosives' Flame Projection Apparatus (see Note, below), the flame projects more than 18 in. beyond the ignition source with valve opened fully, or the flame flashes back and burns at the valve with any degree of valve opening.

   c. Using the Bureau of Explosives' Open Drum Apparatus (see Note, below), there is any significant propagation of flame away from the ignition source.

   d. Using the Bureau of Explosives' Closed Drum Apparatus (see Note, below), there is any explosion of the vapor-air mixture in the drum.

NOTE: Descriptions of the Bureau of Explosives' Flame Projection Apparatus, Open Drum Apparatus, Closed Drum Apparatus, and method of tests may be procured from the Association of American Railroads, Operations and Maintenance Dept., Bureau of Explosives, American Railroad Building, Washington, DC. 20036; 202-293-4048.

Oxidizer (as defined in 49 CFR 173.151)

For the purpose of this regulation, an oxidizer is any material that yields oxygen readily to stimulate the combustion of organic matter (e.g., chlorate, permanganate, inorganic peroxide, or a nitrate).

7.2 CORROSIVITY

7.2.1 Introduction

The corrosivity characteristic, as defined in 40 CFR 261.22, is designed to identify wastes that might pose a hazard to human health or the environment due to their ability to:

1. Mobilize toxic metals if discharged into a landfill environment;

2. Corrode handling, storage, transportation, and management equipment; or

3. Destroy human or animal tissue in the event of inadvertent contact.

In order to identify such potentially hazardous materials, EPA has selected two properties upon which to base the definition of a corrosive waste. These properties are pH and corrosivity toward Type SAE 1020 steel.

The following sections present the regulatory background and the regulation pertaining to the definition of corrosivity. The procedures for measuring pH of aqueous wastes are detailed in Method 9040, Chapter Six. Method 1110, Chapter Eight, describes how to determine whether a waste is corrosive to steel. Use Method 9095, Paint Filter Liquids Test, Chapter Six, to determine free liquid.

7.2.2 Regulatory Definition

The following material has been taken nearly verbatim from the RCRA regulations.

1. A solid waste exhibits the characteristic of corrosivity if a representative sample of the waste has either of the following properties:

   a. It is aqueous and has a pH $\leq$ 2 or $\geq$ 12.5, as determined by a pH meter using either the test method specified in this manual (Method 9040) or an equivalent test method approved by the Administrator under the procedures set forth in Sections 260.20 and 260.21.

   b. It is a liquid and corrodes steel (SAE 1020) at rate > 6.35 mm (0.250 in.) per year at a test temperature of 55°C (130°F), as determined by the test method specified in NACE (National Association of Corrosion Engineers) Standard TM-01-69, as standardized in this manual (Method 1110) or an equivalent test method approved by the Administrator under the procedures set forth in Sections 260.20 and 260.21.

7.3 REACTIVITY

7.3.1 Introduction

The regulation in 40 CFR 261.23 defines reactive wastes to include wastes that have any of the following properties: (1) readily undergo violent chemical change; (2) react violently or form potentially explosive mixtures with water; (3) generate toxic fumes when mixed with water or, in the case of cyanide- or sulfide-bearing wastes, when exposed to mild acidic or basic conditions; (4) explode when subjected to a strong initiating force; (5) explode at normal temperatures and pressures; or (6) fit within the Department of Transportation's forbidden explosives, Class A explosives, or Class B explosives classifications.

This definition is intended to identify wastes that, because of their extreme instability and tendency to react violently or explode, pose a problem at all stages of the waste management process. The definition is to a large extent a paraphrase of the narrative definition employed by the National Fire Protection Association. The Agency chose to rely almost entirely on a descriptive, prose definition of reactivity because most of the available tests for measuring the variegated class of effects embraced by the reactivity definition suffer from a number of deficiencies.

7.3.2 Regulatory Definition

7.3.2.1 Characteristic Of Reactivity Regulation

A solid waste exhibits the characteristic of reactivity if a representative sample of the waste has any of the following properties:

1. It is normally unstable and readily undergoes violent change without detonating.

2. It reacts violently with water.

3. It forms potentially explosive mixtures with water.

4. When mixed with water, it generates toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment.

5. It is a cyanide- or sulfide-bearing waste which, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment. (Interim Guidance for Reactive Cyanide and Reactive Sulfide, Steps 7.3.3 and 7.3.4 below, can be used to detect the presence of reactive cyanide and reactive sulfide in wastes.)

6. It is capable of detonation or explosive reaction if it is subjected to a strong initiating source or if heated under confinement.

7. It is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure.

8. It is a forbidden explosive, as defined in 49 CFR 173.51, or a Class A explosive, as defined in 49 CFR 173.53, or a Class B explosive, as defined in 49 CFR 173.88.

7.3.3 Interim Guidance For Reactive Cyanide

7.3.3.1 The current EPA guidance level is:

Total releasable cyanide: 250 mg HCN/kg waste.

7.3.3.2 Test Method to Determine Hydrogen Cyanide Released from Wastes

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to all wastes, with the condition that wastes that are combined with acids do not form explosive mixtures.

1.2 This method provides a way to determine the specific rate of release of hydrocyanic acid upon contact with an aqueous acid.

1.3 This test measures only the hydrocyanic acid evolved at the test conditions. It is not intended to measure forms of cyanide other than those that are evolvable under the test conditions.

2.0 SUMMARY OF METHOD

2.1 An aliquot of acid is added to a fixed weight of waste in a closed system. The generated gas is swept into a scrubber. The analyte is quantified. The procedure for quantifying the cyanide is Method 9010, Chapter Five, starting with Step 7.2.7 of that method.

3.0 INTERFERENCES

3.1 Interferences are undetermined.

4.0 APPARATUS AND MATERIALS (See Figure 1)

4.1 Round-bottom flask - 500-mL, three-neck, with 24/40 ground-glass joints.

4.2 Gas scrubber - 50 mL calibrated scrubber

4.3 Stirring apparatus - To achieve approximately 30 rpm. This may be either a rotating magnet and stirring bar combination or an overhead motor-driven propeller stirrer.

4.4 Addition funnel - With pressure-equalizing tube and 24/40 ground-glass joint and Teflon sleeve.

4.5 Flexible tubing - For connection from nitrogen supply to apparatus.

4.6 Water-pumped or oil-pumped nitrogen gas - With two-stage regulator.

4.7 Rotometer - For monitoring nitrogen gas flow rate.

4.8 Analytical balance - capable of weighing to 0.001 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Sulfuric acid (0.01N), H_2SO_4. Add 2.8 mL concentrated H_2SO_4 to reagent water and dilute to 1 L. Withdraw 100 mL of this solution and dilute to 1 L to make the 0.01N H_2SO_4.

5.4 Cyanide reference solution, (1000 mg/L). Dissolve approximately 2.5 g of KOH and 2.51 g of KCN in 1 liter of reagent water. Standardize with 0.0192N $AgNO_3$. Cyanide concentration in this solution should be 1 mg/mL.

5.5 Sodium hydroxide solution (1.25N), NaOH. Dissolve 50 g of NaOH in reagent water and dilute to 1 liter with reagent water.

5.6 Sodium hydroxide solution (0.25N), NaOH. Dilute 200 mL of 1.25N sodium hydroxide solution (Step 5.5) to 1 liter with reagent water.

5.7 Silver nitrate solution (0.0192N). Prepare by crushing approximately 5 g of $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh 3.265 g of dried $AgNO_3$, dissolve in reagent water, and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 Samples containing, or suspected of containing, sulfide or a combination of sulfide and cyanide wastes should be collected with a minimum of aeration. The sample bottle should be filled completely, excluding all head space, and stoppered. Analysis should commence as soon as possible, and samples should be kept in a cool, dark place until analysis begins.

6.2 It is suggested that samples of cyanide wastes be tested as quickly as possible. Although they can be preserved by adjusting the sample pH to 12 with strong base, this will cause dilution of the sample, increase the ionic strength, and, possibly, change other physical or chemical

characteristics of the waste which may affect the rate of release of the hydrocyanic acid. Storage of samples should be under refrigeration and in the dark.

6.3 Testing should be performed in a ventilated hood.

7.0 PROCEDURE

7.1 Add 50 mL of 0.25N NaOH solution (Step 5.6) to a calibrated scrubber and dilute with reagent water to obtain an adequate depth of liquid.

7.2 Close the system and adjust the flow rate of nitrogen, using the rotometer. Flow should be 60 mL/min.

7.3 Add 10 g of the waste to be tested to the system.

7.4 With the nitrogen flowing, add enough sulfuric acid to fill the flask half full. Start the 30 minute test period.

7.5 Begin stirring while the acid is entering the round-bottom flask. The stirring speed must remain constant throughout the test.

NOTE: The stirring should not be fast enough to create a vortex.

7.6 After 30 minutes, close off the nitrogen and disconnect the scrubber. Determine the amount of cyanide in the scrubber by Method 9010, Chapter Five, starting with Step 7.2.7 of the method.

NOTE: Delete the "C" and "D" terms from the spectrophotometric procedure calculation and the "E" and "F" terms from the titration procedure calculation in Method 9010. These terms are not necessary for the reactivity determination because the terms determine the amount of cyanide in the entire sample, rather than only in the aliquot taken for analysis.

8.0 CALCULATIONS

8.1 Determine the specific rate of release of HCN, using the following parameters:

X = Concentration of HCN in diluted scrubber solution (mg/L)
(This is obtained from Method 9010.)

L = Volume of solution in scrubber (L)

W = Weight of waste used (kg)

S = Time of measurement (sec.) = Time N_2 stopped - Time N_2 started

R = specific rate of release (mg/kg/sec.) $= \frac{X \cdot L}{W \cdot S}$

Total releasable HCN (mg/kg) = R x S

9.0 METHOD PERFORMANCE

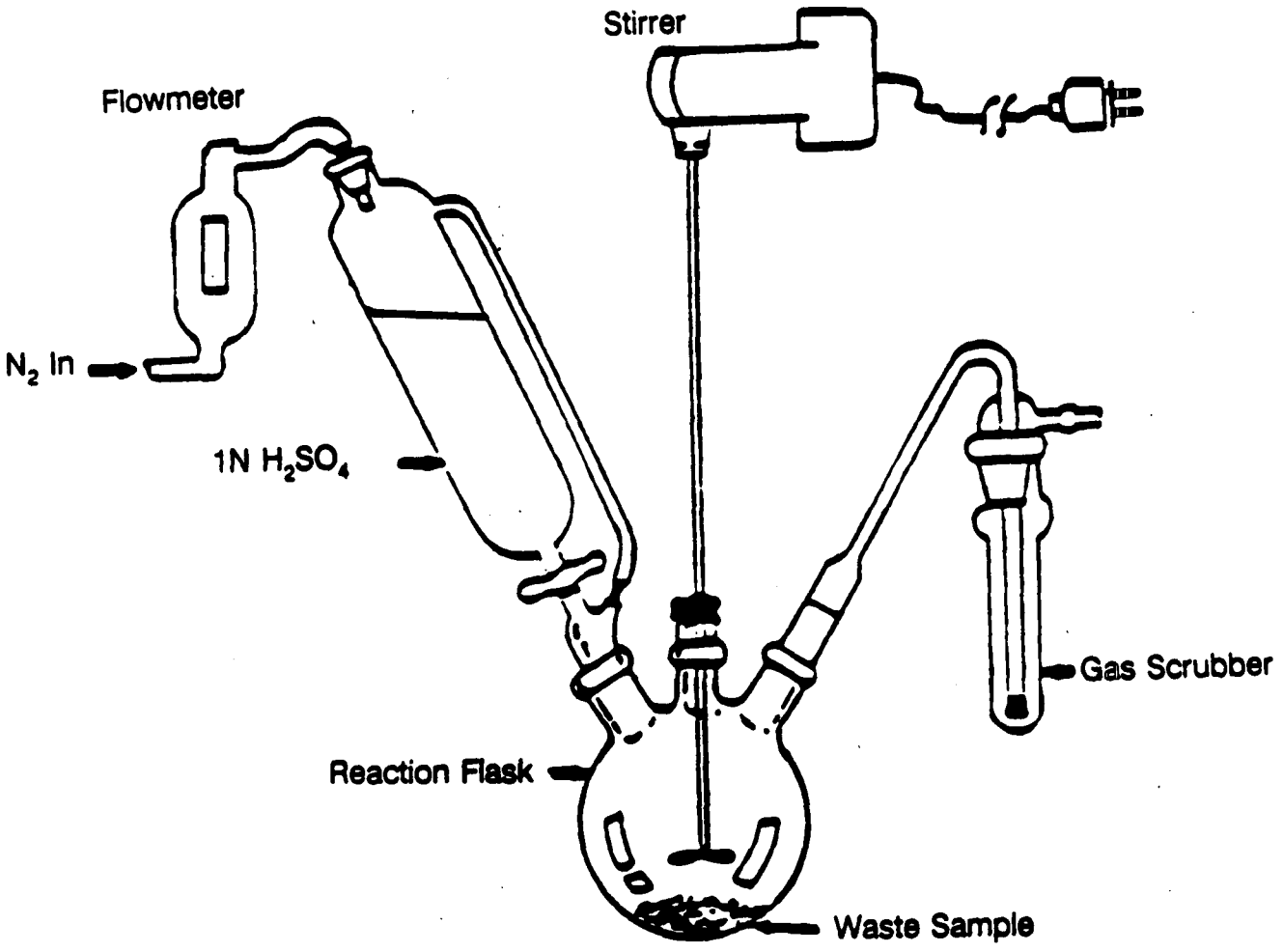
9.1 The operation of the system can be checked and verified using the cyanide reference solution (Step 5.4). Perform the procedure using the reference solution as a sample and determine the percent recovery. Evaluate the standard recovery based on historical laboratory data, as stated in Chapter One.

10.0 REFERENCES

10.1 No references are available at this time.

FIGURE 1.

APPARATUS TO DETERMINE HYDROGEN CYANIDE RELEASED FROM WASTES



7.3.4 Interim Guidance For Reactive Sulfide

7.3.4.1 The current EPA guidance level is:

Total releasable sulfide: 500 mg H_2S/kg waste.

7.3.4.2 Test Method to Determine Hydrogen Sulfide Released from Wastes

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to all wastes, with the condition that waste that are combined with acids do not form explosive mixtures.

1.2 This method provides a way to determine the specific rate of release of hydrogen sulfide upon contact with an aqueous acid.

1.3 This procedure releases only the hydrogen sulfide evolved at the test conditions. It is not intended to measure forms of sulfide other than those that are evolvable under the test conditions.

2.0 SUMMARY OF METHOD

2.1 An aliquot of acid is added to a fixed weight of waste in a closed system. The generated gas is swept into a scrubber. The analyte is quantified. The procedure for quantifying the sulfide is given in Method 9030, Chapter Five, starting with Step 7.3 of that method.

3.0 INTERFERENCES

3.1 Interferences are undetermined.

4.0 APPARATUS AND MATERIALS (See Figure 2)

4.1 Round-bottom flask - 500-mL, three-neck, with 24/40 ground-glass joints.

4.2 Gas scrubber - 50 mL calibrated scrubber.

4.3 Stirring apparatus - To achieve approximately 30 rpm. This may be either a rotating magnet and stirring bar combination or an overhead motor-driven propeller stirrer.

4.4 Addition funnel - With pressure-equalizing tube and 24/40 ground-glass joint and Teflon sleeve.

4.5 Flexible tubing - For connection from nitrogen supply to apparatus.

4.6 Water-pumped or oil-pumped nitrogen gas - With two-stage regulator.

4.7 Rotometer - For monitoring nitrogen gas flow rate.

4.8 Analytical balance - capable of weighing to 0.001 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Sulfuric acid (0.01N), H_2SO_4. Add 2.8 mL concentrated H_2SO_4 to reagent water and dilute to 1 L. Withdraw 100 mL of this solution and dilute to 1 L to make the 0.01N H_2SO_4.

5.4 Sulfide reference solution - Dissolve 4.02 g of $Na_2S \cdot 9H_2O$ in 1.0 L of reagent water. This solution contains 570 mg/L hydrogen sulfide. Dilute this stock solution to cover the analytical range required (100-570 mg/L).

5.5 Sodium hydroxide solution (1.25N), NaOH. Dissolve 50 g of NaOH in reagent water and dilute to 1 L with reagent water.

5.6 Sodium hydroxide solution (0.25N), NaOH. Dilute 200 mL of 1.25N sodium hydroxide solution (Step 5.5) to 1 L with reagent water.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 Samples containing, or suspected of containing, sulfide wastes should be collected with a minimum of aeration. The sample bottle should be filled completely, excluding all head space, and stoppered. Analysis should commence as soon as possible, and samples should be kept in a cool, dark place until analysis begins.

6.2 It is suggested that samples of sulfide wastes be tested as quickly as possible. Although they can be preserved by adjusting the sample pH to 12 with strong base and adding zinc acetate to the sample, these will cause dilution of the sample, increase the ionic strength, and, possibly, change other physical or chemical characteristics of the waste which may affect the rate of release of the hydrogen sulfide. Storage of samples should be under refrigeration and in the dark.

6.3 Testing should be performed in a ventilated hood.

7.0 PROCEDURE

7.1 Add 50 mL of 0.25N NaOH solution to a calibrated scrubber and dilute with reagent water to obtain an adequate depth of liquid.

7.2 Assemble the system and adjust the flow rate of nitrogen, using the rotometer. Flow should be 60 mL/min.

7.3 Add 10 g of the waste to be tested to the system.

7.4 With the nitrogen flowing, add enough sulfuric acid to fill the flask half full, while starting the 30 minute test period.

7.5 Begin stirring while the acid is entering the round-bottom flask. The stirring speed must remain constant throughout the test.

NOTE: The stirring should not be fast enough to create a vortex.

7.6 After 30 minutes, close off the nitrogen and disconnect the scrubber. Determine the amount of sulfide in the scrubber by Method 9030, Chapter Five, starting with Step 7.3 of that method.

7.7 Substitute the following for Step 7.3.2 in Method 9030: The trapping solution must be brought to a pH of 2 before proceeding. Titrate a small aliquot of the trapping solution to a pH 2 end point with 6N HCl and calculate the amount of HCl needed to acidify the entire scrubber solution. Combine the small acidified aliquot with the remainder of the acidified scrubber solution.

8.0 CALCULATIONS

8.1 Determine the specific rate of release of H_2S, using the following parameters:

X = Concentration of H_2S in scrubber (mg/L)
(This is obtained from Method 9030.)

L = Volume of solution in scrubber (L)

W = Weight of waste used (kg)

S = Time of experiment (sec.) = Time N_2 stopped - Time N_2 started

$$R = \text{specific rate of release (mg/kg/sec.)} = \frac{X \cdot L}{W \cdot S}$$

Total releasable H_2S (mg/kg) = R x S

9.0 METHOD PERFORMANCE

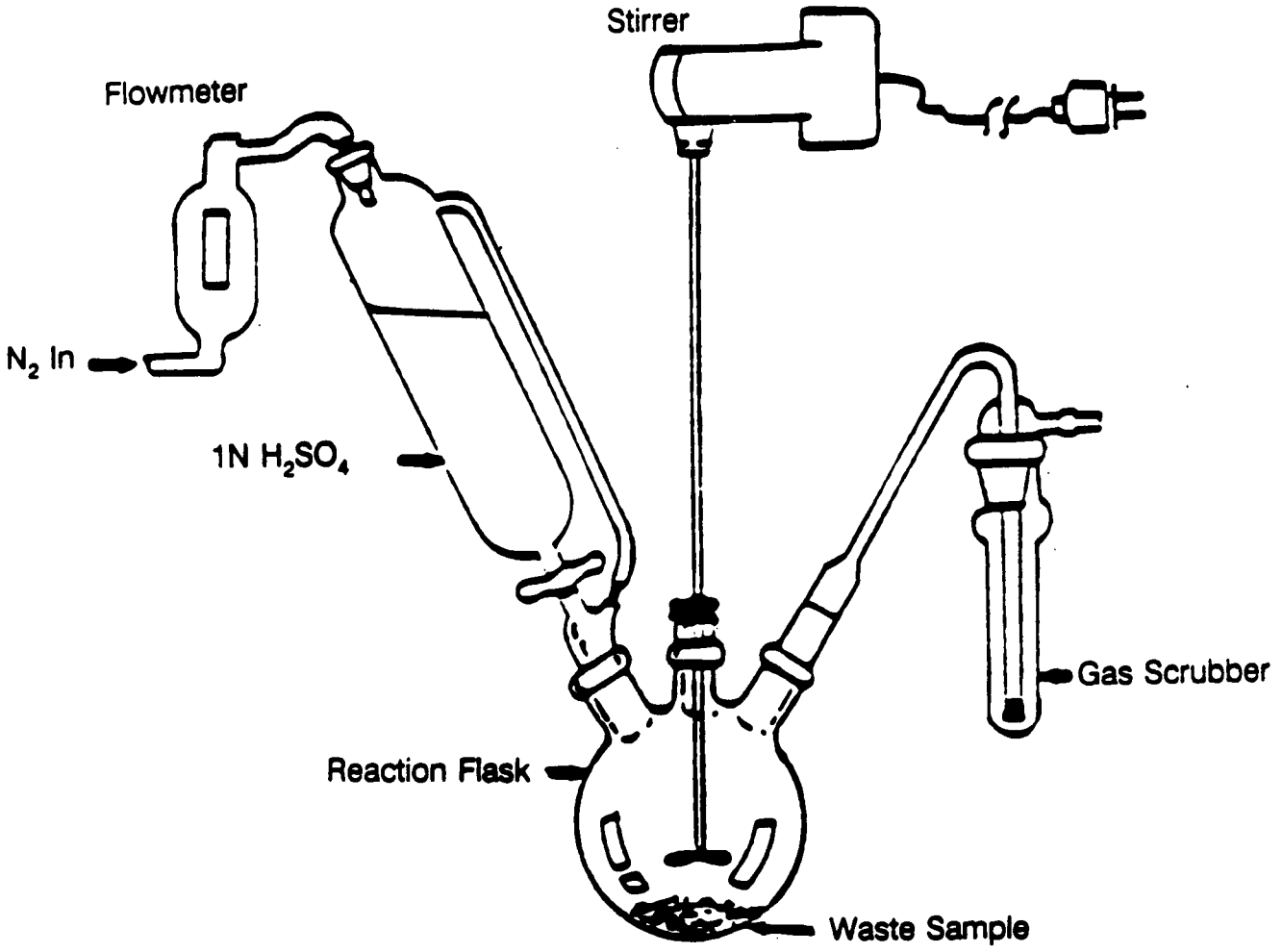
9.1 The operation of the system can be checked and verified using the sulfide reference solution (Step 5.4). Perform the procedure using the reference solution as a sample and determine the percent recovery. Evaluate the standard recovery based on historical laboratory data, as stated in Chapter One.

10.0 REFERENCES

10.1 No references are available at this time.

FIGURE 2.

APPARATUS TO DETERMINE HYDROGEN SULFIDE RELEASED FROM WASTES



7.4 TOXICITY CHARACTERISTIC LEACHING PROCEDURE

7.4.1 Introduction

The Toxicity Characteristic Leaching Procedure (TCLP) is designed to simulate the leaching a waste will undergo if disposed of in a sanitary landfill. This test is designed to simulate leaching that takes place in a sanitary landfill only. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A subsample of a waste is extracted with the appropriate buffered acetic acid solution for 18 $\pm$ 2 hours. The extract obtained from the TCLP (the "TCLP extract") is then analyzed to determine if any of the thresholds established for the 40 Toxicity Characteristic (TC) constituents (listed in Table 7-1) have been exceeded or if the treatment standards established for the constituents listed in 40 CFR §268.41 have been met for the Land Disposal Restrictions (LDR) program. If the TCLP extract contains any one of the TC constituents in an amount equal to or exceeding the concentrations specified in 40 CFR §261.24, the waste possesses the characteristic of toxicity and is a hazardous waste. If the TCLP extract contains LDR constituents in an amount exceeding the concentrations specified in 40 CFR §268.41, the treatment standard for that waste has not been met, and further treatment is necessary prior to land disposal.

7.4.2 Summary of Procedure

The TCLP consists of five steps (refer to Figure 3):

1. Separation Procedure

For liquid wastes (i.e., those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 μm glass fiber filter, is defined as the TCLP extract.

For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis.

2. Particle Size Reduction

Prior to extraction, the solid material must pass through a 9.5-mm (0.375-in.) standard sieve, have a surface area per gram of material equal to or greater than 3.1 cm^2, or, be smaller than 1 cm in its narrowest dimension. If the surface area is smaller or the particle size larger than described above, the solid portion of the waste is prepared for extraction by crushing, cutting, or grinding the waste to the surface area or particle size described above. (Special precautions must be taken if the solids are prepared for organic volatiles extraction.)

3. Extraction of Solid Material

The solid material from Step 2 is extracted for 18 $\pm$ 2 hours with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid

phase of the waste. A special extractor vessel is used when testing for volatile analytes.

4. Final Separation of the Extraction from the Remaining Solid

Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fiber filter. If compatible, the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

5. Testing (Analysis) of TCLP Extract

Inorganic and organic species are identified and quantified using appropriate methods in the 6000, 7000, and 8000 series of methods in this manual or by equivalent methods.

7.4.3 Regulatory Definition

Under the Toxicity Characteristic, a solid waste exhibits the characteristic of toxicity if the TCLP extract from a subsample of the waste contains any of the contaminants listed in Table 7-1 at a concentration greater than or equal to the respective value given in that table. If a waste contains <0.5% filterable solids, the waste itself, after filtering, is considered to be the extract for the purposes of analysis.

Under the Land Disposal Restrictions program, a restricted waste identified in 40 CFR §268.41 may be land disposed only if a TCLP extract of the waste or a TCLP extract of the treatment residue of the waste does not exceed the values shown in Table CCWE of 40 CFR §268.41 for any hazardous constituent listed in Table CCWE for that waste. If a waste contains <0.5% filterable solids, the waste itself, after filtering, is considered to be the extract for the purposes of analysis.

TABLE 7-1.

MAXIMUM CONCENTRATION OF CONTAMINANTS FOR TOXICITY CHARACTERISTIC

Contaminant	Regulatory Level (mg/L)
Arsenic	5.0
Barium	100.0
Benzene	0.5
Cadmium	1.0
Carbon tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
Chromium	5.0
o-Cresol	200.0[1]
m-Cresol	200.0[1]
p-Cresol	200.0[1]
Cresol	200.0[1]
2,4-D	10.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
1,1-Dichloroethylene	0.7
2,4-Dinitrotoluene	0.13[2]
Endrin	0.02
Heptachlor (and its hydroxide)	0.008
Hexachlorobenzene	0.13[2]
Hexachloro-1,3-butadiene	0.5
Hexachloroethane	3.0
Lead	5.0
Lindane	0.4
Mercury	0.2
Methoxychlor	10.0
Methyl ethyl ketone	200.0
Nitrobenzene	2.0
Pentachlorophenol	100.0
Pyridine	5.0[2]
Selenium	1.0
Silver	5.0
Tetrachloroethylene	0.7
Toxaphene	0.5

(continued)

Table 7-1
(continued)

Contaminant	Regulatory Level (mg/L)
Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
2,4,5-TP (Silvex)	1.0
Vinyl chloride	0.2

[1]If o-, m-, and p-cresol concentrations cannot be differentiated, the total cresol (D026) concentration is used. The regulatory level of total cresol is 200 mg/L.

[2]Quantitation limit is greater than the calculated regulatory level. The quantitation limit therefore becomes the regulatory level.

FIGURE 3.

TOXICITY CHARACTERISTIC LEACHATE PROCEDURE FLOWCHART

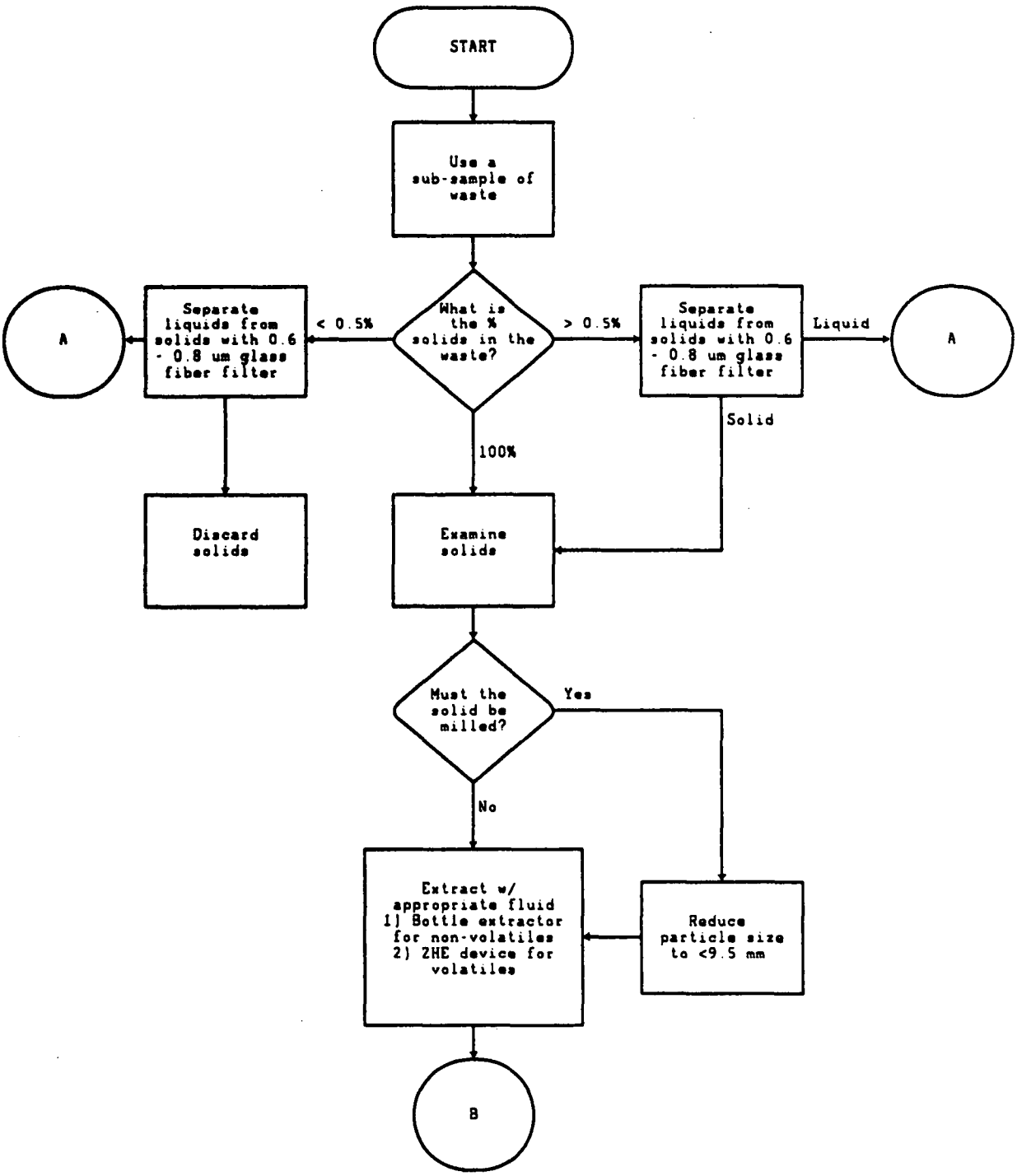
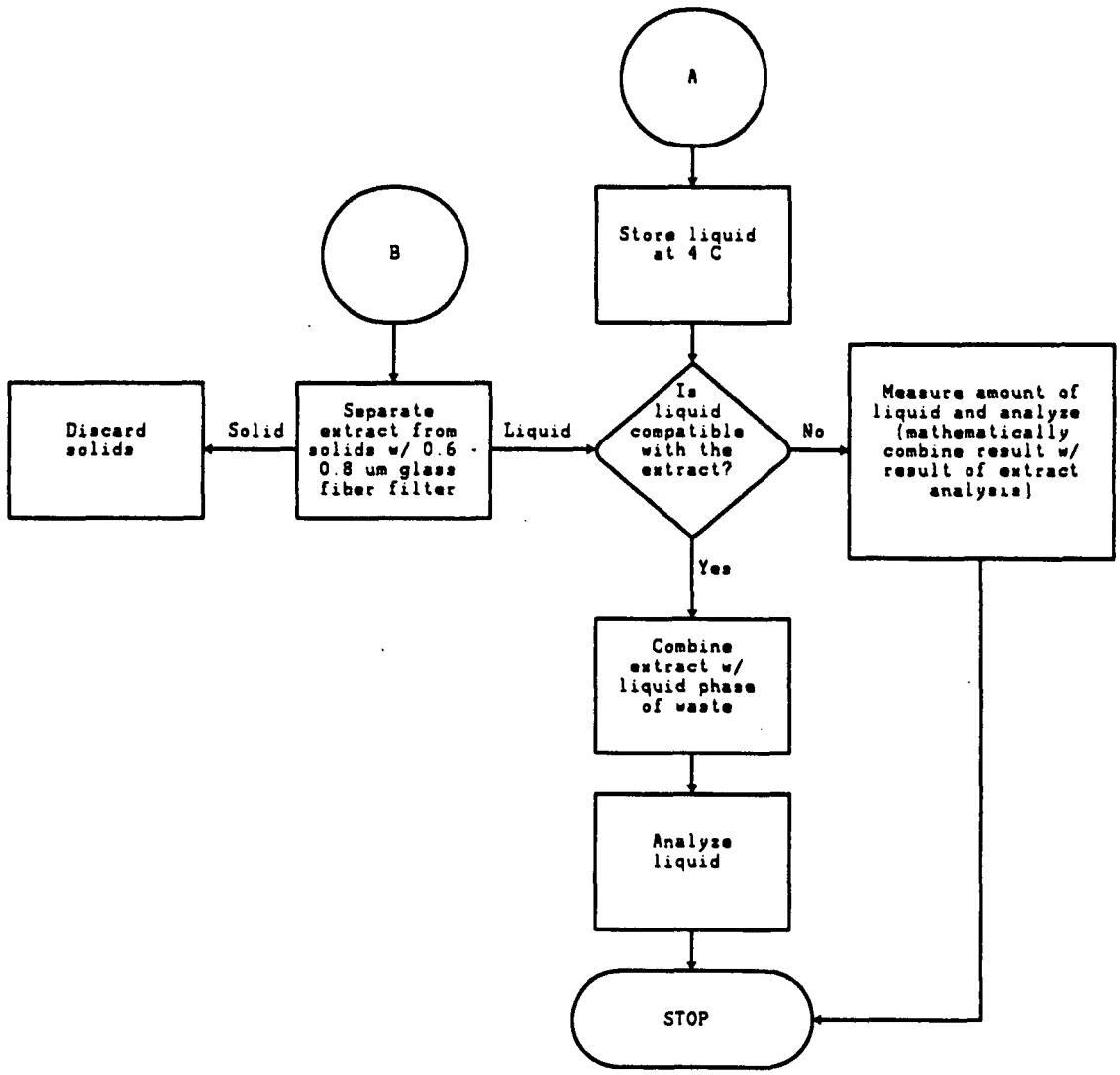


FIGURE 3
(continued)



CHAPTER EIGHT

METHODS FOR DETERMINING CHARACTERISTICS

Methods for determining the characterisitics of Ignitability for liquids, Corrosivity for liquids, and Toxicity are included. Guidance for determining Toxic Gas Generation is found in Chapter Seven, Sections 7.3.3 and 7.3.4.

8.1 Ignitability

The following methods are found in Section 8.1:

Method 1010:	Pensky-Martens Closed-Cup Method for Determining Ignitability
Method 1020A:	Setaflash Closed-Cup Method for Determining Ignitability

METHOD 1010

PENSKY-MARTENS CLOSED-CUP METHOD FOR DETERMINING IGNITABILITY

1.0 SCOPE AND APPLICATION

1.1 Method 1010 uses the Pensky-Martens closed-cup tester to determine the flash point of liquids including those that tend to form a surface film under test conditions. Liquids containing non-filterable, suspended solids shall also be tested using this method.

2.0 SUMMARY OF METHOD

2.1 The sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame ignites the vapor above the sample.

For further information on how to conduct a test by this method, see Reference 1 below.

3.0 METHOD PERFORMANCE

3.1 The Pensky-Martens and Setaflash Closed Testers were evaluated using five industrial waste mixtures and p-xylene. The results of this study are shown below in °F along with other data.

Sample	Pensky-Martens	Setaflash
1[2]	143.7 ± 1.5	139.3 ± 2.1
2[2]	144.7 ± 4.5	129.7 ± 0.6
3[2]	93.7 ± 1.5	97.7 ± 1.2
4[2]	198.0 ± 4.0	185.3 ± 0.6
5[2]	119.3 ± 3.1	122.7 ± 2.5
p-xylene[2]	81.3 ± 1.1	79.3 ± 0.6
p-xylene[3]	77.7 ± 0.5[a]	--
Tanker oil	125, 135	--
Tanker oil	180, 180	--
Tanker oil	110, 110	--
DIBK/xylene	102 ± 4[b]	107

[b]75/25 v/v analyzed by four laboratories.
[a]12 determinations over five-day period.

4.0 REFERENCES

1. D 93-80, Test Methods for Flash Point by Pensky-Martens Closed Tester, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103, 04.09, 1986.

2. Umana, M., Gutknecht, W., Salmons, C., et al., Evaluation of Ignitability Methods (Liquids), EPA/600/S4-85/053, 1985.

3. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

METHOD 1020A

SETAFLASH CLOSED-CUP METHOD FOR DETERMINING IGNITABILITY

1.0 SCOPE AND APPLICATION

1.1 Method 1020 makes use of the Setaflash Closed Tester to determine the flash point of liquids that have flash points between 0° and 110°C (32° and 230°F) and viscosities lower than 150 stokes at 25°C (77°F).

1.2 The procedure may be used to determine whether a material will or will not flash at a specified temperature or to determine the finite temperature at which a material will flash.

1.3 Liquids that tend to form surface films under test conditions or those that contain non-filterable suspended solids shall be tested for ignitability using Method 1010 (Pensky-Martens Closed-Cup).

2.0 SUMMARY OF METHOD

2.1 By means of a syringe, 2-mL of sample is introduced through a leak-proof entry port into the tightly closed Setaflash Tester or directly into the cup which has been brought to within 3°C (5°F) below the expected flash point.

2.2 As a flash/no-flash test, the expected flash-point temperature may be a specification (e.g., 60°C). For specification testing, the temperature of the apparatus is raised to the precise temperature of the specification flash point by slight adjustment of the temperature dial. After 1 minute, a test flame is applied inside the cup and note is taken as to whether the test sample flashes or not. If a repeat test is necessary, a fresh sample should be used.

2.3 For a finite flash management, the temperature is sequentially increased through the anticipated range, the test flame being applied at 5°C (9°F) intervals until a flash is observed. A repeat determination is then made using a fresh sample, starting the test at the temperature of the last interval before the flash point of the material and making tests at increasing 0.5°C (1°F) intervals.

For further information on how to conduct a test with this method, see Reference 1 below.

3.0 METHOD PERFORMANCE

See Method 1010.

4.0 REFERENCES

1. D-3278-78, Test Method for Flash Point of Liquids by Setaflash Closed Tester, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

2. Umana, M., Gutknecht, W., Salmons, C., et al., Evaluation of Ignitability Methods (Liquids), EPA/600/S4-85/053, 1985.

3. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

8.2 Corrosivity

The following method is found in Section 8.2:

Method 1110: Corrosivity Toward Steel

METHOD 1110

CORROSIVITY TOWARD STEEL

1.0 SCOPE AND APPLICATION

1.1 Method 1110 is used to measure the corrosivity toward steel of both aqueous and nonaqueous liquid wastes.

2.0 SUMMARY OF METHOD

2.1 This test exposes coupons of SAE Type 1020 steel to the liquid waste to be evaluated and, by measuring the degree to which the coupon has been dissolved, determines the corrosivity of the waste.

3.0 INTERFERENCES

3.1 In laboratory tests, such as this one, corrosion of duplicate coupons is usually reproducible to within 10%. However, large differences in corrosion rates may occasionally occur under conditions where the metal surfaces become passivated. Therefore, at least duplicate determinations of corrosion rate should be made.

4.0 APPARATUS AND MATERIALS

4.1 An apparatus should be used, consisting of a kettle or flask of suitable size (usually 500 to 5,000 mL), a reflux condenser, a thermowell and temperature regulating device, a heating device (mantle, hot plate, or bath), and a specimen support system. A typical resin flask set up for this type of test is shown in Figure 1.

4.2 The supporting device and container shall be constructed of materials that are not affected by, or cause contamination of, the waste under test.

4.3 The method of supporting the coupons will vary with the apparatus used for conducting the test, but it should be designed to insulate the coupons from each other physically and electrically and to insulate the coupons from any metallic container or other device used in the test. Some common support materials include glass, fluorocarbon, or coated metal.

4.4 The shape and form of the coupon support should ensure free contact with the waste.

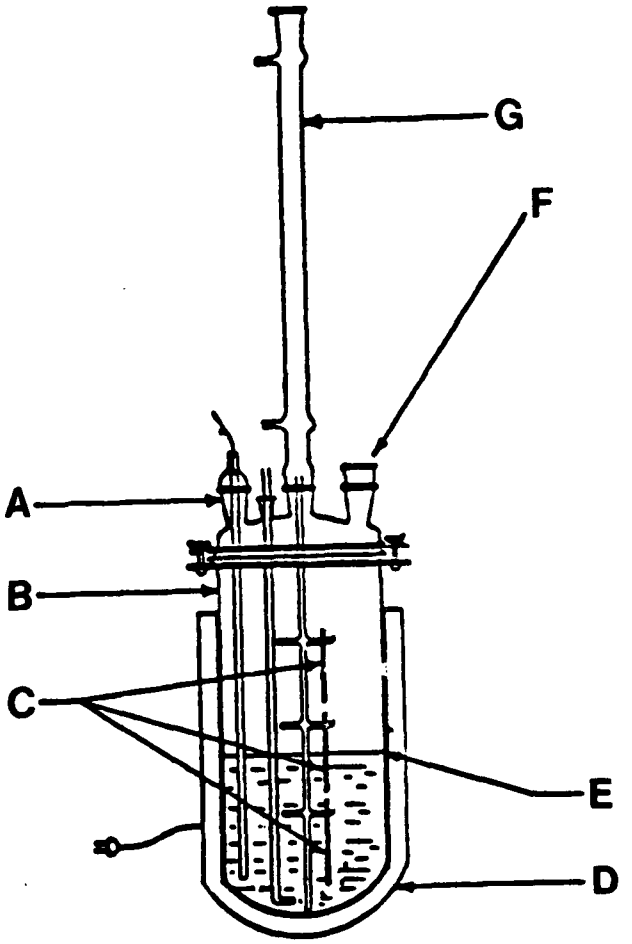


Figure 1. Typical resin flask that can be used as a versatile and convenient apparatus to conduct simple immersion tests. Configuration of the flask top is such that more sophisticated apparatus can be added as required by the specific test being conducted. A = thermowell, B = resin flask, C = specimens hung on supporting device, D = heating mantle, E = liquid interface, F = opening in flask for additional apparatus that may be required, and G = reflux condenser.

4.5 A circular specimen of SAE 1020 steel of about 3.75 cm (1.5 in.) diameter is a convenient shape for a coupon. With a thickness of approximately 0.32 cm (0.125 in.) and a 0.80-cm (0.4-in.)-diameter hole for mounting, these specimens will readily pass through a 45/50 ground-glass joint of a distillation kettle. The total surface area of a circular specimen is given by the following equation:

$$A = 3.14/2(D^2-d^2) + (t)(3.14)(D) + (t)(3.14)(d)$$

where:

t = thickness.
D = diameter of the specimen.
d = diameter of the mounting hole.

If the hole is completely covered by the mounting support, the last term in the equation, (t)(3.14)(d), is omitted.

4.5.1 All coupons should be measured carefully to permit accurate calculation of the exposed areas. An area calculation accurate to ±1% is usually adequate.

4.5.2 More uniform results may be expected if a substantial layer of metal is removed from the coupons prior to testing the corrosivity of the waste. This can be accomplished by chemical treatment (pickling), by electrolytic removal, or by grinding with a coarse abrasive. At least 0.254 mm (0.0001 in.) or 2-3 mg/cm^2 should be removed. Final surface treatment should include finishing with #120 abrasive paper or cloth. Final cleaning consists of scrubbing with bleach-free scouring powder, followed by rinsing in distilled water and then in acetone or methanol, and finally by air-drying. After final cleaning, the coupon should be stored in a desiccator until used.

4.5.3 The minimum ratio of volume of waste to area of the metal coupon to be used in this test is 40 mL/cm^2.

5.0 REAGENTS

5.1 Sodium hydroxide (NaOH), (20%): Dissolves 200 g NaOH in 800 mL Type II water and mix well.

5.2 Zinc dust.

5.3 Hydrochloric acid (HCl): Concentrated.

5.4 Stannous chloride ($SnCl_2$).

5.5 Antimony chloride ($SbCl_3$).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples should be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

7.0 PROCEDURE

7.1 Assemble the test apparatus as described in Paragraph 4.0, above.

7.2 Fill the container with the appropriate amount of waste.

7.3 Begin agitation at a rate sufficient to ensure that the liquid is kept well mixed and homogeneous.

7.4 Using the heating device, bring the temperature of the waste to 55°C (130°F).

7.5 An accurate rate of corrosion is not required; only a determination as to whether the rate of corrosion is less than or greater than 6.35 mm per year is required. A 24-hr test period should be ample to determine whether or not the rate of corrosion is >6.35 mm per year.

7.6 In order to determine accurately the amount of material lost to corrosion, the coupons have to be cleaned after immersion and prior to weighing. The cleaning procedure should remove all products of corrosion while removing a minimum of sound metal. Cleaning methods can be divided into three general categories: mechanical, chemical, and electrolytic.

7.6.1 Mechanical cleaning includes scrubbing, scraping, brushing, and ultrasonic procedures. Scrubbing with a bristle brush and mild abrasive is the most popular of these methods. The others are used in cases of heavy corrosion as a first step in removing heavily encrusted corrosion products prior to scrubbing. Care should be taken to avoid removing sound metal.

7.6.2 Chemical cleaning implies the removal of material from the surface of the coupon by dissolution in an appropriate solvent. Solvents such as acetone, dichloromethane, and alcohol are used to remove oil, grease, or resinous materials and are used prior to immersion to remove the products of corrosion. Solutions suitable for removing corrosion from the steel coupon are:

Solution	Soaking Time	Temperature
20% NaOH + 200 g/L zinc dust	5 min	Boiling
or		
Conc. HCl + 50 g/L $SnCl_2$ + 20 g/L $SbCl_3$	Until clean	Cold

7.6.3 Electrolytic cleaning should be preceded by scrubbing to remove loosely adhering corrosion products. One method of electrolytic cleaning that can be employed uses:

Solution:	50 g/L H_2SO_4
Anode:	Carbon or lead
Cathode:	Steel coupon
Cathode current density:	20 amp/cm^2 (129 amp/$in.^2$)
Inhibitor:	2 cc organic inhibitor/liter
Temperature:	74°C (165°F)
Exposure Period:	3 min.

NOTE: Precautions must be taken to ensure good electrical contact with the coupon to avoid contamination of the cleaning solution with easily reducible metal ions and to ensure that inhibitor decomposition has not occurred. Instead of a proprietary inhibitor, 0.5 g/L of either diorthotolyl thiourea or quinolin ethiodide can be used.

7.7 Whatever treatment is employed to clean the coupons, its effect in removing sound metal should be determined by using a blank (i.e., a coupon that has not been exposed to the waste). The blank should be cleaned along with the test coupon and its waste loss subtracted from that calculated for the test coupons.

7.8 After corroded specimens have been cleaned and dried, they are reweighed. The weight loss is employed as the principal measure of corrosion. Use of weight loss as a measure of corrosion requires making the assumption that all weight loss has been due to generalized corrosion and not localized pitting. In order to determine the corrosion rate for the purpose of this regulation, the following formula is used:

$$\text{Corrosion Rate (mmpy)} = \frac{\text{weight loss x 11.145}}{\text{area x time}}$$

where: weight loss is in milligrams,
area in square centimeters,
time in hours, and
corrosion rate in millimeters per year (mmpy).

8.0 QUALITY CONTROL

8.1 All quality control data should be filed and available for auditing.

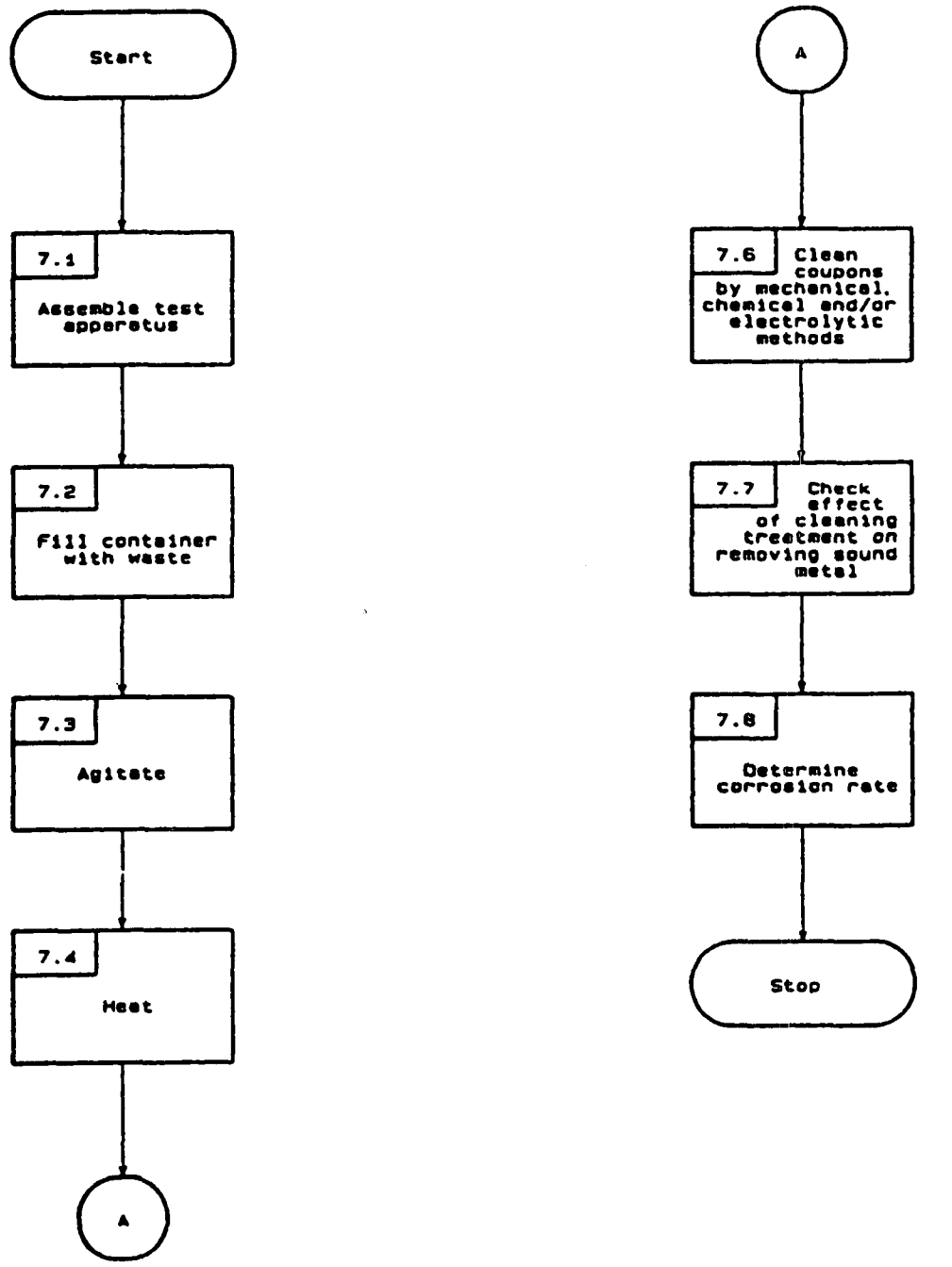
8.2 Duplicate samples should be analyzed on a routine basis.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. National Association of Corrosion Engineers, "Laboratory Corrosion Testing of Metals for the Process Industries," NACE Standard TM-01-69 (1972 Revision), NACE, 3400 West Loop South, Houston, TX 77027.



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8.3 Reactivity

Refer to guidance given in Chapter Seven, especially Section 7.3.3 and 7.3.4.

8.4 Toxicity

The following methods are found in Section 8.4:

Method 1310A:	Extraction Procedure (EP) Toxicity Test Method and Structural Integrity Test
Method 1311:	Toxicity Characteristic Leaching Procedure

*U.S. G.P.O.;1995-386-824:33251

METHOD 1310A

EXTRACTION PROCEDURE (EP) TOXICITY TEST METHOD AND STRUCTURAL INTEGRITY TEST

1.0 SCOPE AND APPLICATION

1.1 This method is an interim method to determine whether a waste exhibits the characteristic of Extraction Procedure Toxicity.

1.2 The procedure may also be used to simulate the leaching which a waste may undergo if disposed of in a sanitary landfill. Method 1310 is applicable to liquid, solid, and multiphase samples.

2.0 SUMMARY OF METHOD

2.1 If a representative sample of the waste contains > 0.5% solids, the solid phase of the sample is ground to pass a 9.5 mm sieve and extracted with deionized water which is maintained at a pH of 5 $\pm$ 0.2, with acetic acid. Wastes that contain < 0.5% filterable solids are, after filtering, considered to be the EP extract for this method. Monolithic wastes which can be formed into a cylinder 3.3 cm (dia) x 7.1 cm, or from which such a cylinder can be formed which is representative of the waste, may be evaluated using the Structural Integrity Procedure instead of being ground to pass a 9.5-mm sieve.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Extractor - For purposes of this test, an acceptable extractor is one that will impart sufficient agitation to the mixture to (1) prevent stratification of the sample and extraction fluid and (2) ensure that all sample surfaces are continuously brought into contact with well-mixed extraction fluid. Examples of suitable extractors are shown in Figures 1-3 of this method and are available from: Associated Designs & Manufacturing Co., Alexandria, Virginia; Glas-Col Apparatus Co., Terre Haute, Indiana; Millipore, Bedford, Massachusetts; and Rexnard, Milwaukee, Wisconsin.

4.2 pH meter or pH controller - Accurate to 0.05 pH units with temperature compensation.

4.3 Filter holder - Capable of supporting a 0.45-μm filter membrane and of withstanding the pressure needed to accomplish separation. Suitable filter holders range from simple vacuum units to relatively complex systems that can exert up to 5.3 kg/cm^3 (75 psi) of pressure. The type of filter holder used depends upon the properties of the mixture to be filtered. Filter holders known to EPA and deemed suitable for use are listed in Table 1.

4.4 Filter membrane - Filter membrane suitable for conducting the required filtration shall be fabricated from a material that (1) is not physically changed by the waste material to be filtered and (2) does not absorb or leach the chemical species for which a waste's EP extract will be analyzed. Table 2 lists filter media known to the agency to be suitable for solid waste testing.

4.4.1 In cases of doubt about physical effects on the filter, contact the filter manufacturer to determine if the membrane or the prefilter is adversely affected by the particular waste. If no information is available, submerge the filter in the waste's liquid phase. A filter that undergoes visible physical change after 48 hours (i.e., curls, dissolves, shrinks, or swells) is unsuitable for use.

4.4.2 To test for absorption or leaching by the filter:

4.4.2.1 Prepare a standard solution of the chemical species of interest.

4.4.2.2 Analyze the standard for its concentration of the chemical species.

4.4.2.3 Filter the standard and reanalyze. If the concentration of the filtrate differs from that of the original standard, then the filter membrane leaches or absorbs one or more of the chemical species and is not usable in this test method.

4.5 Structural integrity tester - A device meeting the specifications shown in Figure 4 and having a 3.18-cm (1.25-in) diameter hammer weighing 0.33 kg (0.73 lb) with a free fall of 15.24 cm (6 in) shall be used. This device is available from Associated Design and Manufacturing Company, Alexandria, VA 22314, as Part No. 125, or it may be fabricated to meet these specifications.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Acetic acid (0.5N), CH_3COOH. This can be made by diluting concentrated glacial acetic acid (17.5N) by adding 57 mL glacial acetic acid to 1,000 mL of water and diluting to 2 liters. The glacial acetic acid must be of high purity and monitored for impurities.

5.4 Analytical standards should be prepared according to the applicable analytical methods.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Preservatives must not be added to samples.

6.3 Samples can be refrigerated if it is determined that refrigeration will not affect the integrity of the sample.

7.0 PROCEDURE

7.1 If the waste does not contain any free liquid, go to Step 7.9. If the sample is liquid or multiphase, continue as follows. Weigh filter membrane and prefilter to $\pm$ 0.01 g. Handle membrane and prefilters with blunt curved-tip forceps or vacuum tweezers, or by applying suction with a pipet.

7.2 Assemble filter holder, membranes, and prefilters following the manufacturer's instructions. Place the 0.45-μm membrane on the support screen and add prefilters in ascending order of pore size. Do not prewet filter membrane.

7.3 Weigh out a representative subsample of the waste (100 g minimum).

7.4 Allow slurries to stand, to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration.

7.5 Wet the filter with a small portion of the liquid phase from the waste or from the extraction mixture. Transfer the remaining material to the filter holder and apply vacuum or gentle pressure (10-15 psi) until all liquid passes through the filter. Stop filtration when air or pressurizing gas moves through the membrane. If this point is not reached under vacuum or gentle pressure, slowly increase the pressure in 10-psi increments to 75 psi. Halt filtration when liquid flow stops. This liquid will constitute part or all of the extract (refer to Step 7.16). The liquid should be refrigerated until time of analysis.

NOTE: Oil samples or samples containing oil are treated in exactly the same way as any other sample. The liquid portion of the sample is filtered and treated as part of the EP extract. If the liquid portion of the sample will not pass through the filter (usually the case with heavy oils or greases), it should be carried through the EP extraction as a solid.

7.6 Remove the solid phase and filter media and, while not allowing them to dry, weigh to $\pm$ 0.01 g. The wet weight of the residue is determined by calculating the weight difference between the weight of the filters (Step 7.1) and the weight of the solid phase and the filter media.

7.7 The waste will be handled differently from this point on, depending on whether it contains more or less than 0.5% solids. If the sample appears to have < 0.5% solids, determine the percent solids exactly (see Note below) by the following procedure:

7.7.1 Dry the filter and residue at 80°C until two successive weighings yield the same value.

7.7.2 Calculate the percent solids, using the following equation:

$$\frac{\text{weight of filtered solid and filters} - \text{tared weight of filters}}{\text{initial weight of waste material}} \times 100 = \% \text{ solids}$$

NOTE: This procedure is used only to determine whether the solid must be extracted or whether it can be discarded unextracted. It is not used in calculating the amount of water or acid to use in the extraction step. Do not extract solid material that has been dried at 80°C. A new sample will have to be used for extraction if a percent solids determination is performed.

7.8 If the solid constitutes < 0.5% of the waste, discard the solid and proceed immediately to Step 7.17, treating the liquid phase as the extract.

7.9 The solid material obtained from Step 7.5 and all materials that do not contain free liquids shall be evaluated for particle size. If the solid material has a surface area per g of material ≥ 3.1 cm^2 or passes through a 9.5-mm (0.375-in.) standard sieve, the operator shall proceed to Step 7.11. If the surface area is smaller or the particle size larger than specified above, the solid material shall be prepared for extraction by crushing, cutting, or grinding the material so that it passes through a 9.5-mm (0.375-in.) sieve or, if the material is in a single piece, by subjecting the material to the "Structural Integrity Procedure" described in Step 7.10.

7.10 Structural Integrity Procedure (SIP)

7.10.1 Cut a 3.3-cm diameter by 7.1-cm long cylinder from the waste material. If the waste has been treated using a fixation process, the waste may be cast in the form of a cylinder and allowed to cure for 30 days prior to testing.

7.10.2 Place waste into sample holder and assemble the tester. Raise the hammer to its maximum height and drop. Repeat 14 additional times.

7.10.3 Remove solid material from tester and scrape off any particles adhering to sample holder. Weigh the waste to the nearest 0.01 g and transfer it to the extractor.

7.11 If the sample contains > 0.5% solids, use the wet weight of the solid phase (obtained in Step 7.6) to calculate the amount of liquid and acid to employ for extraction by using the following equation:

$$W = W_f - W_t$$

where :

W = Wet weight in g of solid to be charged to extractor.

W_f = Wet weight in g of filtered solids and filter media.

W_t = Weight in g of tared filters.

If the waste does not contain any free liquids, 100 g of the material will be subjected to the extraction procedure.

7.12 Place the appropriate amount of material (refer to Step 7.11) into the extractor and add 16 times its weight with water.

7.13 After the solid material and water are placed in the extractor, the operator shall begin agitation and measure the pH of the solution in the extractor. If the pH is > 5.0, the pH of the solution should be decreased to 5.0 ± 0.2 by slowly adding 0.5N acetic acid. If the pH is ≤ 5.0, no acetic acid should be added. The pH of the solution should be monitored, as described below, during the course of the extraction, and, if the pH rises above 5.2, 0.5N acetic acid should be added to bring the pH down to 5.0 ± 0.2. However, in no event shall the aggregate amount of acid added to the solution exceed 4 mL of acid per g of solid. The mixture should be agitated for 24 hours and maintained at 20-40°C (68-104°F) during this time. It is recommended that the operator monitor and adjust the pH during the course of the extraction with a device such as the Type 45-A pH Controller, manufactured by Chemtrix, Inc., Hillsboro, Oregon 97123, or its equivalent, in conjunction with a metering pump and reservoir of 0.5N acetic acid. If such a system is not available, the following manual procedure shall be employed.

NOTE: Do not add acetic acid too quickly. Lowering the pH to below the target concentration of 5.0 could affect the metal concentrations in the leachate.

7.13.1 A pH meter should be calibrated in accordance with the manufacturer's specifications.

7.13.2 The pH of the solution should be checked, and, if necessary, 0.5 N acetic acid should be manually added to the extractor until the pH reaches 5.0 ± 0.2. The pH of the solution should be adjusted at 15-, 30-, and 60-minute intervals, moving to the next longer interval if the pH does not have to be adjusted > 0.5 pH units.

7.13.3 The adjustment procedure should be continued for at least 6 hours.

7.13.4 If, at the end of the 24-hour extraction period, the pH of the solution is not below 5.2 and the maximum amount of acid (4 mL per g of solids) has not been added, the pH should be adjusted to 5.0 ± 0.2 and the extraction continued for an additional 4 hours, during which the pH should be adjusted at 1-hour intervals.

7.14 At the end of the extraction period, water should be added to the extractor in an amount determined by the following equation:

$$V = (20)(W) - 16(W) - A$$

where:

V = mL water to be added.

W = Weight in g of solid charged to extractor.

A = mL of 0.5N acetic acid added during extraction.

7.15 The material in the extractor should be separated into its component liquid and solid phases in the following manner:

7.15.1 Allow slurries to stand to permit the solid phase to settle (wastes that are slow to settle may be centrifuged prior to filtration) and set up the filter apparatus (refer to Steps 4.3 and 4.4).

7.15.2 Wet the filter with a small portion of the liquid phase from the waste or from the extraction mixture. Transfer the remaining material to the filter holder and apply vacuum or gentle pressure (10-15 psi) until all liquid passes through the filter. Stop filtration when air or pressurizing gas moves through the membrane. If this point is not reached under vacuum or gentle pressure, slowly increase the pressure in 10-psi increments to 75 psi. Halt filtration when liquid flow stops.

7.16 The liquids resulting from Steps 7.5 and 7.15 should be combined. This combined liquid (or waste itself, if it has < 0.5% solids, as noted in Step 7.8) is the extract.

7.17 The extract is then prepared and analyzed using the appropriate analytical methods described in Chapters Three and Four of this manual.

NOTE: If the EP extract includes two phases, concentration of contaminants is determined by using a simple weighted average. For example: An EP extract contains 50 mL of oil and 1,000 mL of an aqueous phase. Contaminant concentrations are determined for each phase. The final contamination concentration is taken to be:

$$\frac{\left(50 \times \text{contaminant conc. in oil}\right) + \left(1{,}000 \times \text{contaminant conc. of aqueous phase}\right)}{1050}$$

NOTE: In cases where a contaminant was not detected, use the MDL in the calculation. For example, if the MDL in the oily phase is 100 mg/L and 1 mg/L in the aqueous phase, the reporting limit would be 6 mg/L (rounded to the nearest mg). If the regulatory threshold is 5 mg/L, the waste may be EP toxic and results of the analysis are inconclusive.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 All quality control measures described in Chapter One and in the referenced analytical methods should be followed.

9.0 METHOD PERFORMANCE

9.1 The data tabulated in Table 3 were obtained from records of state and contractor laboratories and are intended to show the precision of the entire method (1310 plus analysis method).

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

3. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. EPA-APPROVED FILTER HOLDERS

Manufacturer	Size	Model No.	Comments
Vacuum Filters			
Gelman	47 mm	4011	
Nalgene	500 mL	44-0045	Disposable plastic unit, including prefilter, filter pads, and reservoir; can be used when solution is to be analyzed for inorganic constituents.
Nuclepore	47 mm	410400	
Millipore	47 mm	XX10 047 00	
Pressure Filters			
Nuclepore	142 mm	425900	
Micro Filtration Systems	142 mm	302300	
Millipore	142 mm	YT30 142 HW	

TABLE 2. EPA-APPROVED FILTRATION MEDIA

Supplier	Filter to be used for aqueous systems	Filter to be used for organic systems
Coarse prefilter		
Gelman	61631, 61635	61631, 61635
Nuclepore	210907, 211707	210907, 211707
Millipore	AP25 035 00, AP25 127 50	AP25 035 00, AP25 127 50
Medium prefilters		
Gelman	61654, 61655	
Nuclepore	210905, 211705	210905, 211705
Millipore	AP20 035 00, AP20 124 50	AP20 035 00, AP20 124 50
Fine prefilters		
Gelman	64798, 64803	64798, 64803
Nuclepore	210903, 211703	210903, 211703
Millipore	AP15 035 00, AP15 124 50	AP15 035 00, AP15 124 50
Fine filters (0.45 μm)		
Gelman	63069, 66536	60540 or 66149, 66151
Pall	NX04750, NX14225	
Nuclepore	142218	142218[a]
Millipore	HAWP 047 00, HAWP 142 50	FHUP 047 00, FHLP 142 50
Selas	83485-02, 83486-02	83485-02, 83486-02

[a]Susceptible to decomposition by certain polar organic solvents.

TABLE 3. PRECISIONS OF EXTRACTION-ANALYSIS PROCEDURES FOR SEVERAL ELEMENTS

Element	Sample Matrix	Analysis Method	Laboratory Replicates
Arsenic	1. Auto fluff	7060	1.8, 1.5 µg/L
	2. Barrel sludge	7060	0.9, 2.6 µg/L
	3. Lumber treatment company sediment	7060	28, 42 mg/L
Barium	1. Lead smelting emission control dust	6010	0.12, 0.12 mg/L
	2. Auto fluff	7081	791, 780 µg/L
	3. Barrel sludge	7081	422, 380 µg/L
Cadmium	1. Lead smelting emission control dust	3010/7130	120, 120 mg/L
	2. Wastewater treatment sludge from electroplating	3010/7130	360, 290 mg/L
	3. Auto fluff	7131	470, 610 µg/L
	4. Barrel sludge	7131	1100, 890 µg/L
	5. Oil refinery tertiary pond sludge	7131	3.2, 1.9 µg/L
Chromium	1. Wastewater treatment sludge from electroplating	3010/7190	1.1, 1.2 mg/L
	2. Paint primer	7191	61, 43 µg/L
	3. Paint primer filter	7191	--
	4. Lumber treatment company sediment	7191	0.81, 0.89 mg/L
	5. Oil refinery tertiary pond sludge	7191	--
Mercury	1. Barrel sludge	7470	0.15, 0.09 µg/L
	2. Wastewater treatment sludge from electroplating	7470	1.4, 0.4 µg/L
	3. Lead smelting emission control dust	7470	0.4, 0.4 µg/L

TABLE 3 (Continued)

Element	Sample Matrix	Analysis Method	Laboratory Replicates
Lead	1. Lead smelting emission control dust	3010/7420	940, 920 mg/L
	2. Auto fluff	7421	1540, 1490 µg/L
	3. Incinerator ash	7421	1000, 974 µg/L
	4. Barrel sludge	7421	2550, 2800 µg/L
	5. Oil refinery tertiary pond sludge	7421	31, 29 µg/L
Nickel	1. Sludge	7521	2260, 1720 µg/L
	2. Wastewater treatment sludge from electroplating	3010/7520	130, 140 mg/L
Chromium(VI)	1. Wastewater treatment sludge from electroplating	7196	18, 19 µg/L

FIGURE 1.
EXTRACTOR

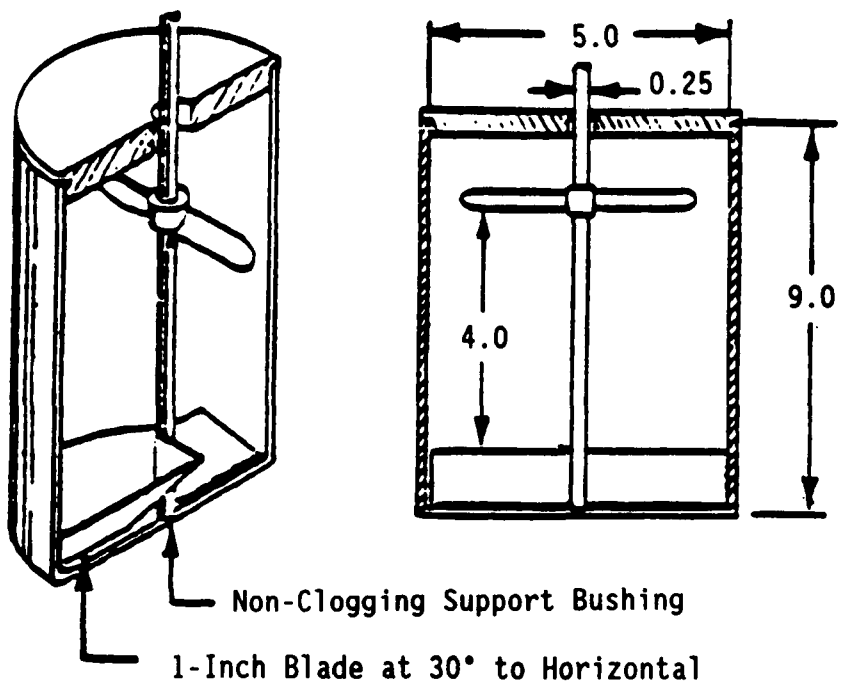


FIGURE 2.
ROTARY EXTRACTOR

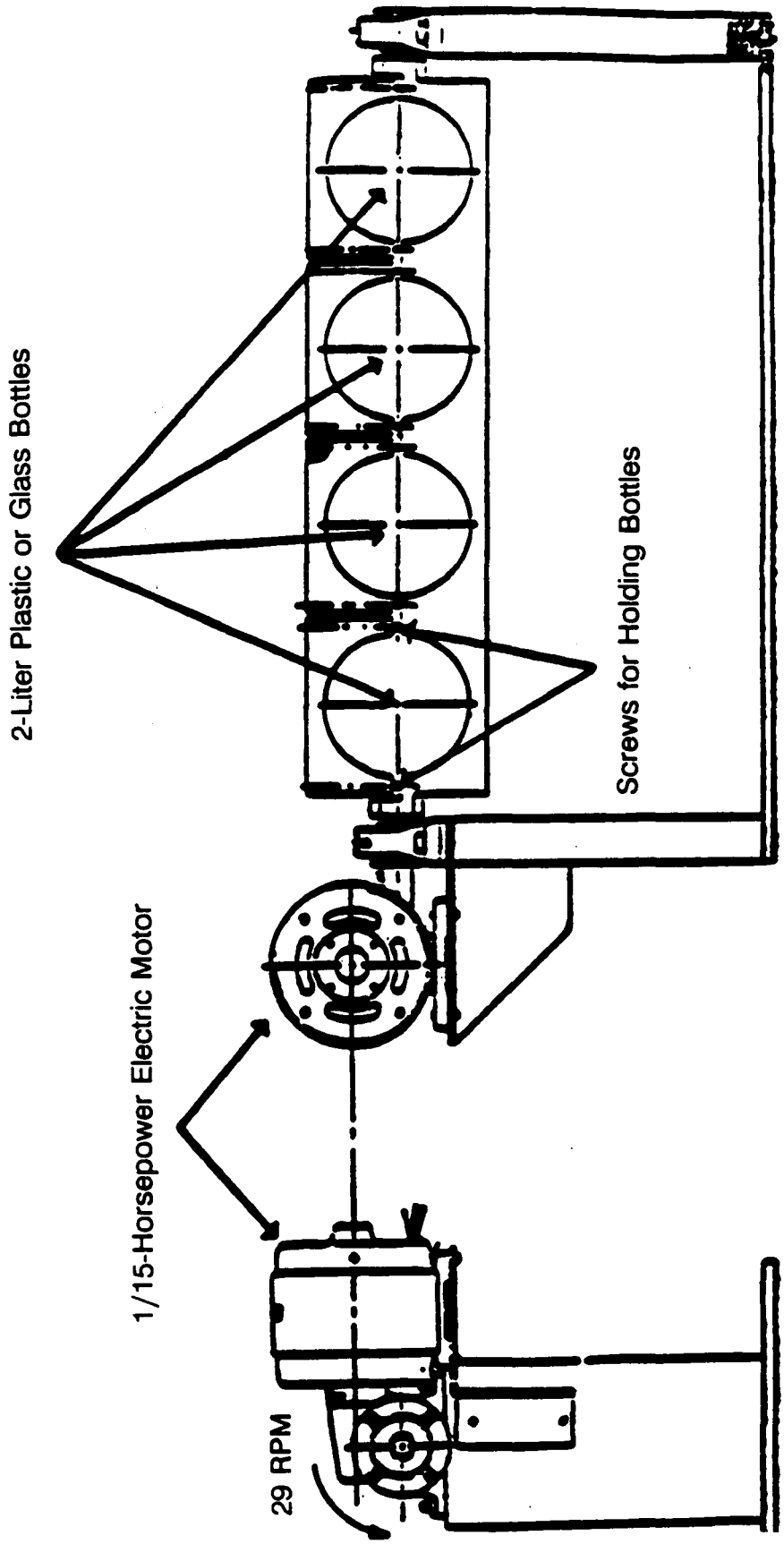


FIGURE 3.
EPRI EXTRACTOR

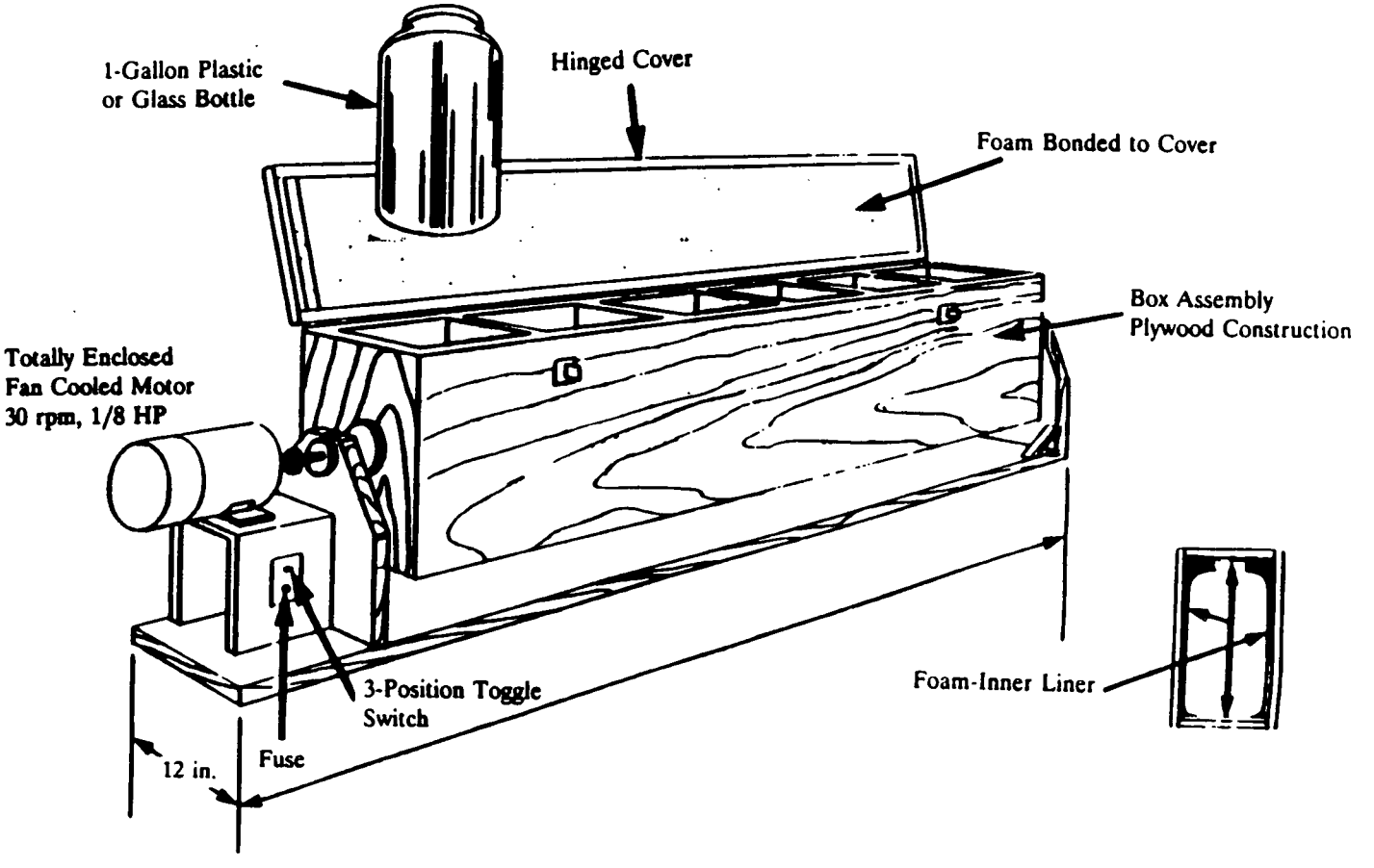
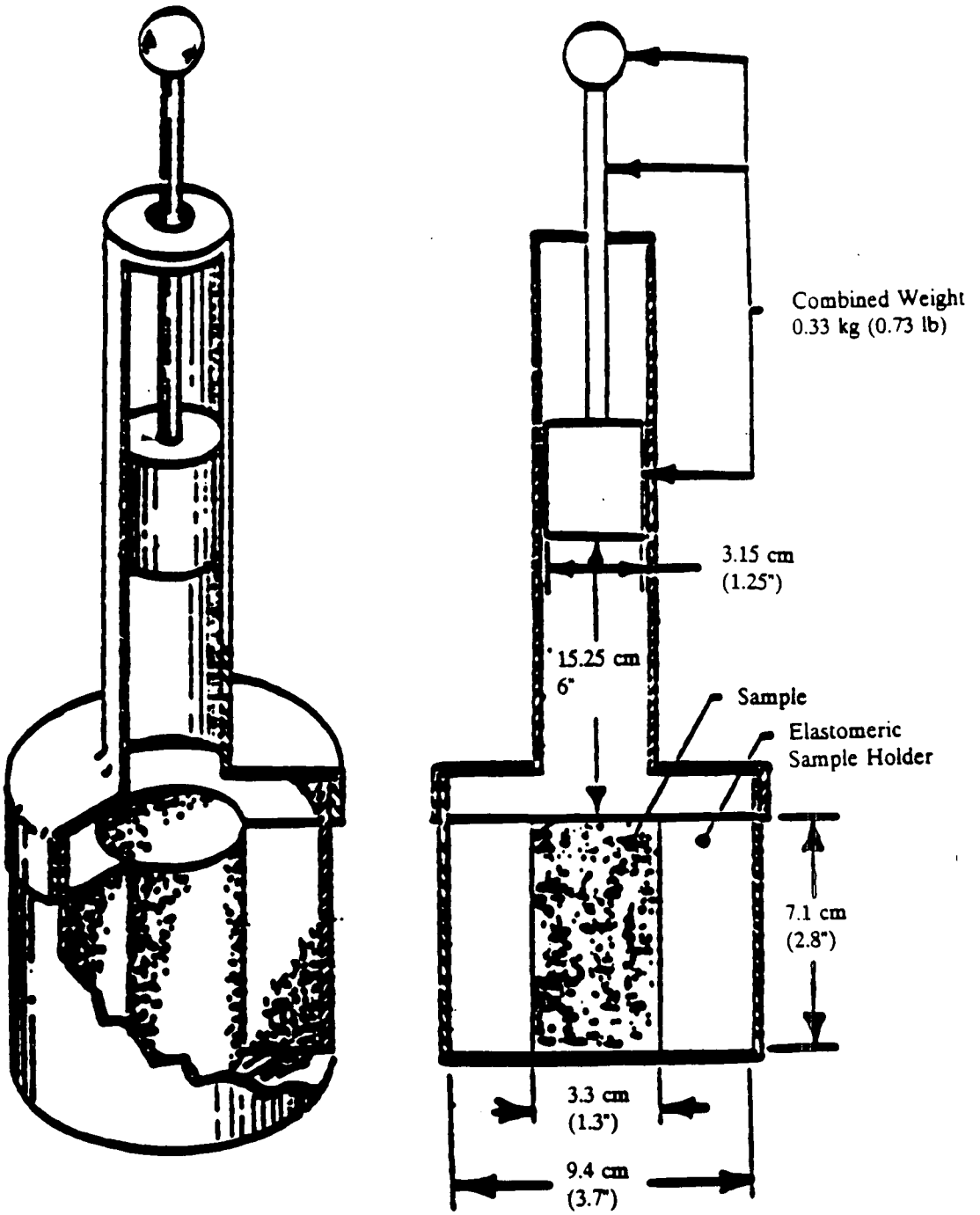
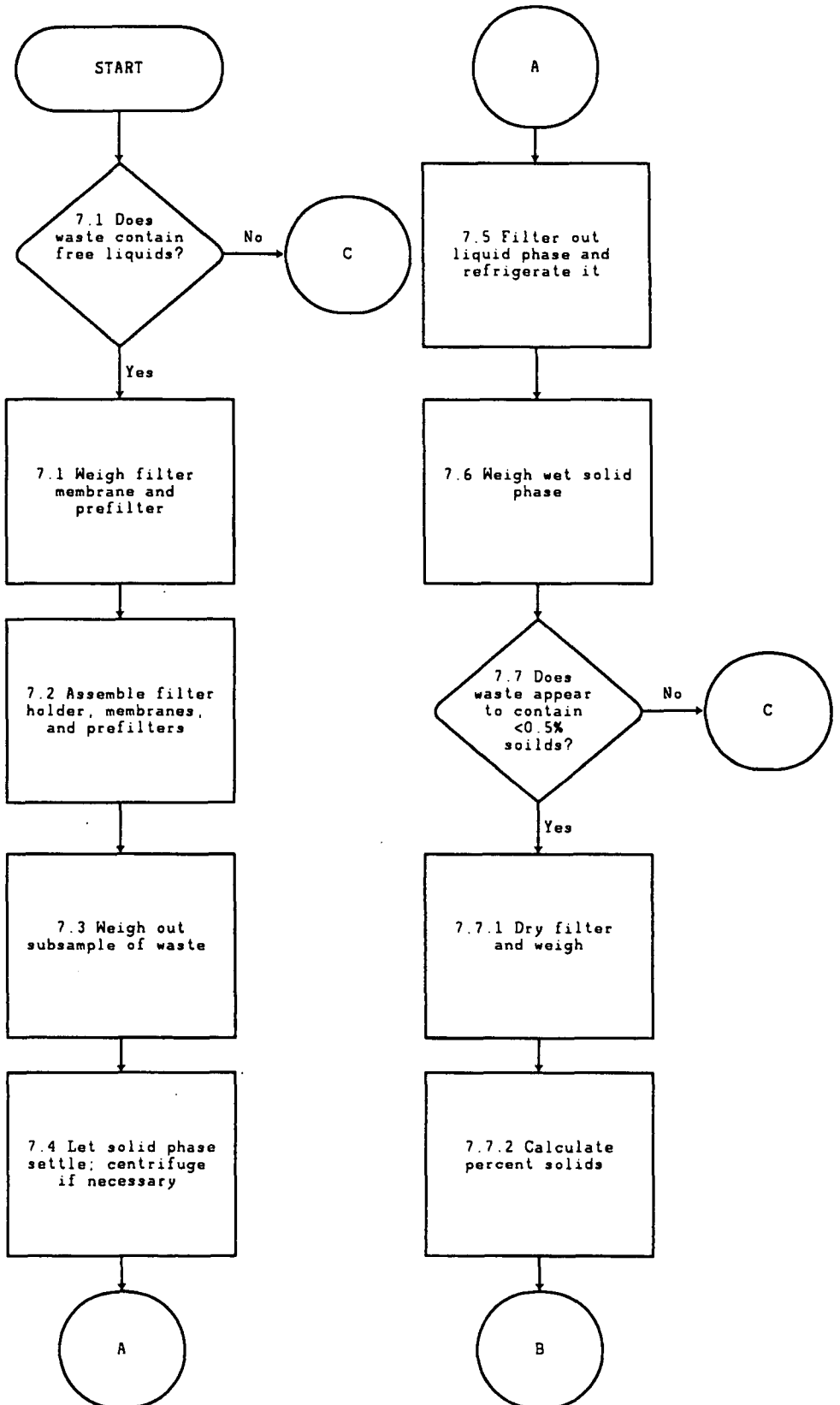
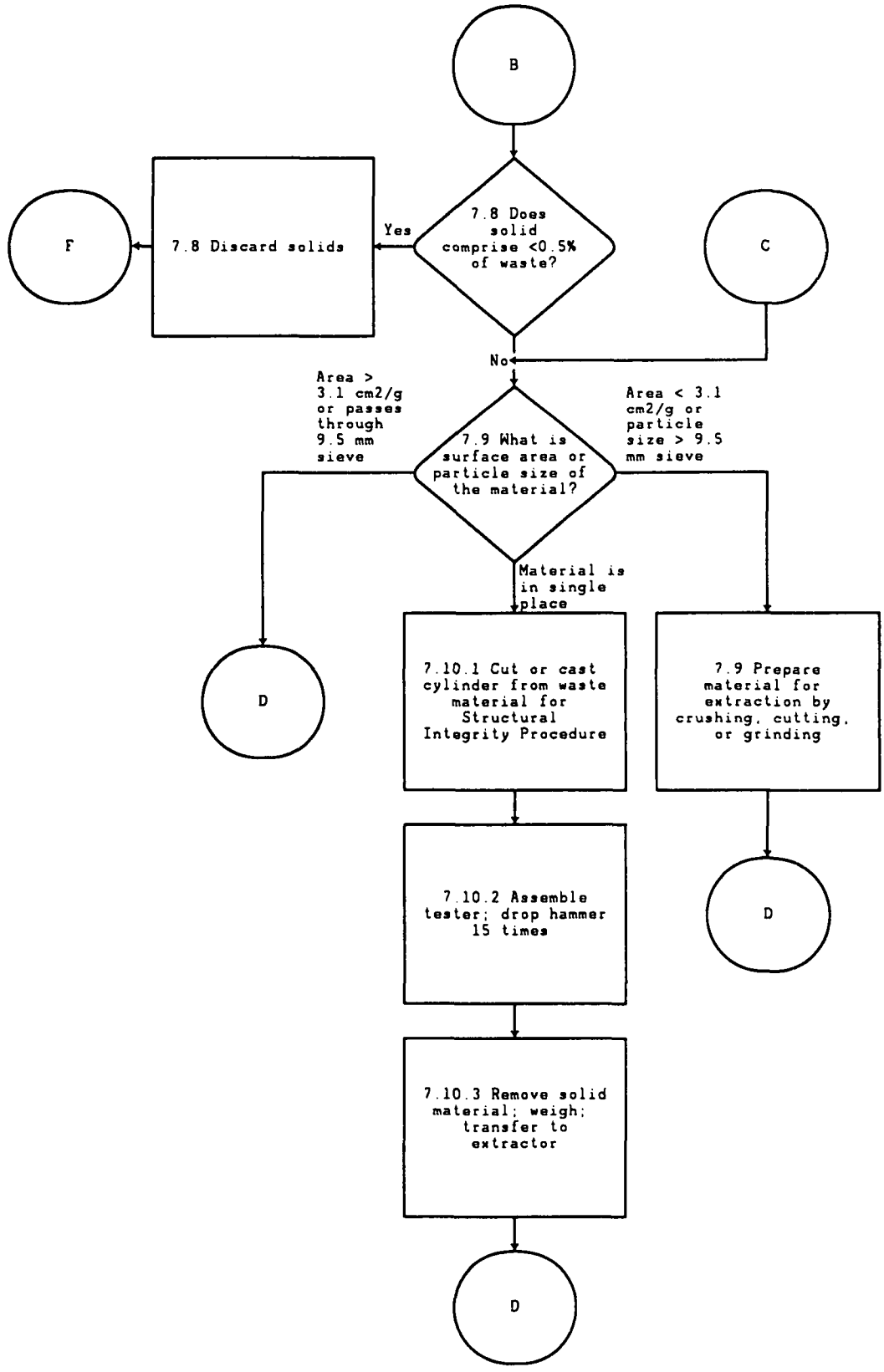
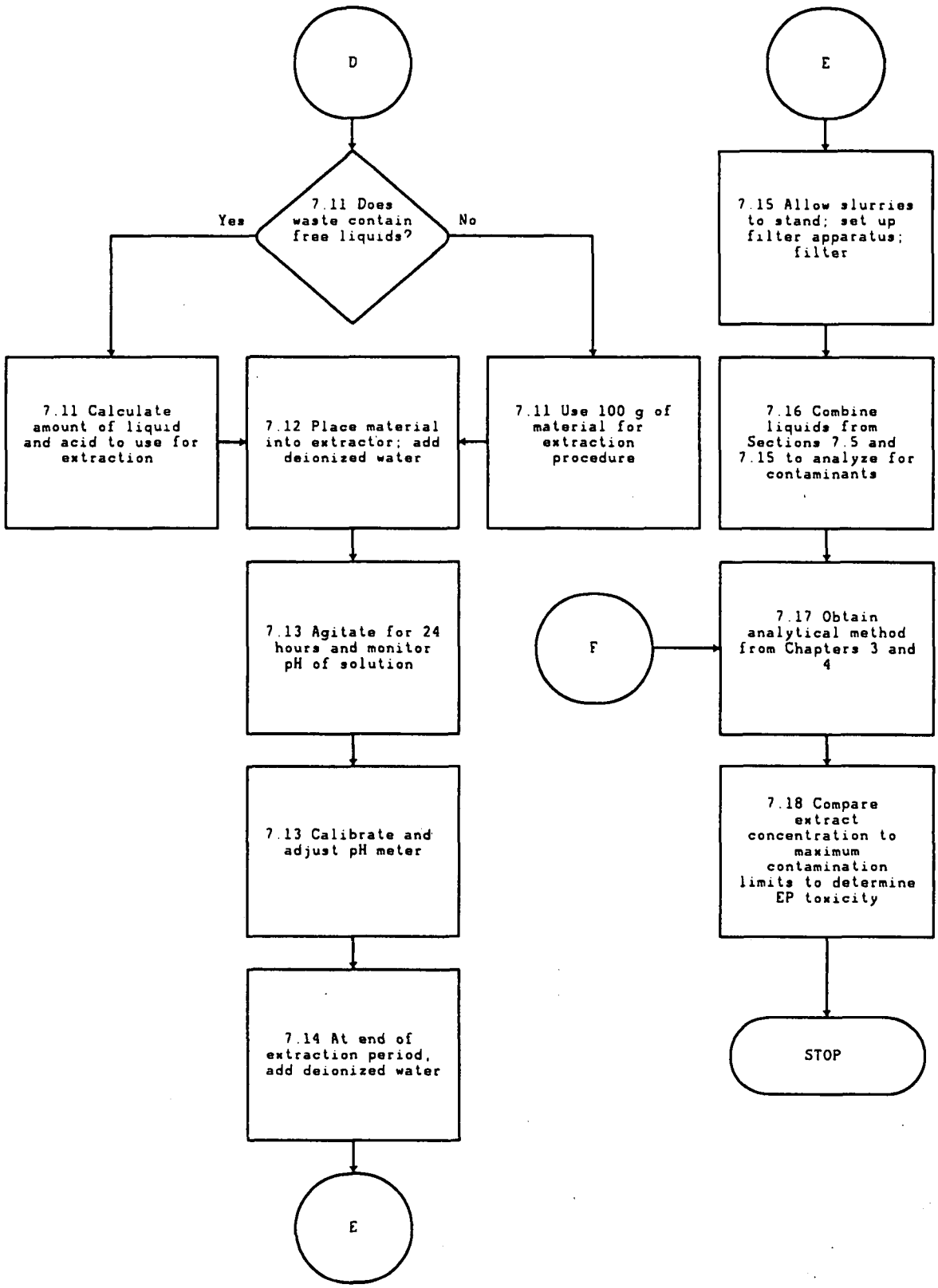


FIGURE 4.
COMPACTION TESTER




START
7.1 Does waste contain free liquids?
No
C
Yes
7.1 Weigh filter membrane and prefilter
7.2 Assemble filter holder, membranes, and prefilters
7.3 Weigh out subsample of waste
7.4 Let solid phase settle; centrifuge if necessary
A
A
7.5 Filter out liquid phase and refrigerate it
7.6 Weigh wet solid phase
7.7 Does waste appear to contain <0.5% soilds?
No
C
Yes
7.7.1 Dry filter and weigh
7.7.2 Calculate percent solids
B


B
7.8 Does solid comprise <0.5% of waste?
Yes
7.8 Discard solids
F
C
No
7.9 What is surface area or particle size of the material?
Area > 3.1 cm2/g or passes through 9.5 mm sieve
Area < 3.1 cm2/g or particle size > 9.5 mm sieve
Material is in single place
D
7.10.1 Cut or cast cylinder from waste material for Structural Integrity Procedure
7.9 Prepare material for extraction by crushing, cutting, or grinding
7.10.2 Assemble tester; drop hammer 15 times
D
7.10.3 Remove solid material; weigh; transfer to extractor
D


D
7.11 Does waste contain free liquids?
Yes
No
7.11 Calculate amount of liquid and acid to use for extraction
7.12 Place material into extractor; add deionized water
7.11 Use 100 g of material for extraction procedure
7.13 Agitate for 24 hours and monitor pH of solution
7.13 Calibrate and adjust pH meter
7.14 At end of extraction period, add deionized water
E
E
7.15 Allow slurries to stand; set up filter apparatus; filter
7.16 Combine liquids from Sections 7.5 and 7.15 to analyze for contaminants
F
7.17 Obtain analytical method from Chapters 3 and 4
7.18 Compare extract concentration to maximum contamination limits to determine EP toxicity
STOP

METHOD 1311

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.

1.2 If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run.

1.3 If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.4 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level.

2.0 SUMMARY OF METHOD

2.1 For liquid wastes (i.e., those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 μm glass fiber filter, is defined as the TCLP extract.

2.2 For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fiber filter.

2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at 30 ± 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.2 Extraction Vessels

4.2.1 Zero-Headspace Extraction Vessel (ZHE). This device is for use only when the waste is being tested for the mobility of volatile analytes (i.e., those listed in Table 1). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel (see Section 4.3.1). The vessels shall have an internal volume of 500-600 mL, and be equipped to accommodate a 90-110 mm filter. The devices contain VITON®[1] O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see Section 7.3) refers to pounds per square inch (psi), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

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[1] VITON® is a trademark of Du Pont.

4.2.2 Bottle Extraction Vessel. When the waste is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see Section 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Section 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.3 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.3.1 Zero-Headspace Extractor Vessel (ZHE): When the waste is evaluated for volatiles, the zero-headspace extraction vessel described in Section 4.2.1 is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psi).

NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.3.2 Filter Holder: When the waste is evaluated for other than volatile analytes, any filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered (see Section 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10%) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are shown in Table 4.

4.3.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used only when evaluating the mobility of metals. Borosilicate glass bottles are recommended for use over other types of glass bottles, especially when inorganics are analytes of concern.

4.4 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8 μm, or equivalent. Filters known to EPA which meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1 L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters: The meter should be accurate to $\pm$ 0.05 units at 25 °C.

4.6 ZHE Extract Collection Devices: TEDLAR®[2] bags or glass, stainless steel or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device. The devices listed are recommended for use under the following conditions:

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., <1% of total waste), the TEDLAR® bag or a 600 mL syringe should be used to collect and combine the initial liquid and solid extract.

4.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., >1% of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100% solid) or has no significant solid phase (is 100% liquid), either the TEDLAR® bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g., a positive displacement or peristaltic pump, a gas tight syringe, pressure filtration unit (see Section 4.3.2), or other ZHE device).

4.8 Laboratory Balance: Any laboratory balance accurate to within $\pm$ 0.01 grams may be used (all weight measurements are to be within $\pm$ 0.1 grams).

4.9 Beaker or Erlenmeyer flask, glass, 500 mL.

4.10 Watchglass, appropriate diameter to cover beaker or Erlenmeyer flask.

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[2] TEDLAR® is a registered trademark of Du Pont.

4.11 Magnetic stirrer.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analyte(s) of interest. For nonvolatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.2.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 grams of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.2.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.2.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 $\pm$ 5 degrees C, bubble a contaminant-free inert gas (e.g. nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-headspace and seal with a Teflon-lined septum and cap.

5.3 Hydrochloric acid (1N), HCl, made from ACS reagent grade.

5.4 Nitric acid (1N), HNO_3, made from ACS reagent grade.

5.5 Sodium hydroxide (1N), NaOH, made from ACS reagent grade.

5.6 Glacial acetic acid, CH_3CH_2OOH, ACS reagent grade.

5.7 Extraction fluid.

5.7.1 Extraction fluid # 1: Add 5.7 mL glacial CH_3CH_2OOH to 500 mL of reagent water (See Section 5.2), add 64.3 mL of 1N NaOH, and dilute to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 4.93 $\pm$ 0.05.

5.7.2 Extraction fluid # 2: Dilute 5.7 mL glacial CH_3CH_2OOH with reagent water (See Section 5.2) to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 $\pm$ 0.05.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.8 Analytical standards shall be prepared according to the appropriate analytical method.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples shall be collected using an appropriate sampling plan.

6.2 The TCLP may place requirements on the minimal size of the field sample, depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for preliminary evaluation of which extraction fluid is to be used for the nonvolatile analyte extraction procedure. Another aliquot may be needed to actually conduct the nonvolatile extraction (see Section 1.4 concerning the use of this extract for volatile organics). If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more sample just in case something goes wrong with the initial attempt to conduct the test.

6.3 Preservatives shall not be added to samples before extraction.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the waste is to be evaluated for volatile analytes, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4 °C. Samples should be opened only immediately prior to extraction).

6.6 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs (see Section 7.2.14 if precipitation occurs). Extracts should be preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See Section 8.0 (QA requirements) for acceptable sample and extract holding times.

7.0 PROCEDURE

7.1 Preliminary Evaluations

Perform preliminary TCLP evaluations on a minimum 100 gram aliquot of waste. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include: (1) determination of the percent solids (Section 7.1.1); (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (Section 7.1.2); (3) determination of whether the solid portion of the waste requires particle size reduction (Section 7.1.3); and (4) determination of which of the two extraction fluids are to be used for the nonvolatile TCLP extraction of the waste (Section 7.1.4).

7.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids) proceed to Section 7.1.3.

7.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.1.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.1.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.1.7 Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and

subtract it from the sample weight determined in Section 7.1.1.5 to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.1.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Section 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Section 7.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in Section 7.1.1.5 or 7.1.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (Section 7.1.1.9)}}{\text{Total weight of waste (Section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2 If the percent solids determined in Section 7.1.1.9 is equal to or greater than 0.5%, then proceed either to Section 7.1.3 to determine whether the solid material requires particle size reduction or to Section 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in Section 7.1.1.9 is less than 0.5%, then proceed to Section 7.2.9 if the

nonvolatile TCLP is to be performed and to Section 7.3 with a fresh portion of the waste if the volatile TCLP is to be performed.

7.1.2.1 Remove the solid phase and filter from the filtration apparatus.

7.1.2.2 Dry the filter and solid phase at 100 ± 20 °C until two successive weighing yield the same value within ± 1%. Record the final weight.

NOTE: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

7.1.2.3 Calculate the percent dry solids as follows:

$$\text{Percent dry solids} = \frac{\text{(Wt. of dry waste + filter) - tared wt. of filter}}{\text{Initial wt. of waste (Section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5%, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed, and to Section 7.3 if the volatile TCLP is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile TCLP is to be performed, return to the beginning of this Section (7.1) and, with a fresh portion of waste, determine whether particle size reduction is necessary (Section 7.1.3) and determine the appropriate extraction fluid (Section 7.1.4). If only the volatile TCLP is to be performed, see the note in Section 7.1.4.

7.1.3 Determination of whether the waste requires particle size reduction (particle size is reduced during this step): Using the solid portion of the waste, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see Section 7.3.6).

NOTE: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

7.1.4 Determination of appropriate extraction fluid: If the solid content of the waste is greater than or equal to 0.5% and if the sample will be extracted for nonvolatile constituents (Section 7.2), determine the appropriate fluid (Section 5.7) for the nonvolatiles extraction as follows:

NOTE: TCLP extraction for volatile constituents uses only extraction fluid #1 (Section 5.7.1). Therefore, if TCLP extraction for nonvolatiles is not required, proceed to Section 7.3.

7.1.4.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500 mL beaker or Erlenmeyer flask.

7.1.4.2 Add 96.5 mL of reagent water to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use extraction fluid #1. Proceed to Section 7.2.

7.1.4.3 If the pH from Section 7.1.4.2 is >5.0, add 3.5 mL 1N HCl, slurry briefly, cover with a watchglass, heat to 50 °C, and hold at 50 °C for 10 minutes.

7.1.4.4 Let the solution cool to room temperature and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2. Proceed to Section 7.2.

7.1.5 If the aliquot of the waste used for the preliminary evaluation (Sections 7.1.1 - 7.1.4) was determined to be 100% solid at Section 7.1.1.1, then it can be used for the Section 7.2 extraction (assuming at least 100 grams remain), and the Section 7.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in Section 7.1.1.7, then another aliquot shall be used for the volatile extraction procedure in Section 7.3. The aliquot of the waste subjected to the procedure in Section 7.1.1.7 might be appropriate for use for the Section 7.2 extraction if an adequate amount of solid (as determined by Section 7.1.1.9) was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to Section 7.2.10 of the nonvolatile TCLP extraction.

7.2 Procedure When Volatiles are not Involved

A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample (percent solids, See Section 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all

of the analyses required. If the amount of extract generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid, see Section 7.1.1), weigh out a subsample of the waste (100 gram minimum) and proceed to Section 7.2.9.

7.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.2.3 to 7.2.8.

7.2.3 Pre-weigh the container that will receive the filtrate.

7.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Section 4.4).

NOTE: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.

7.2.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight. If the waste contains <0.5% dry solids (Section 7.1.2), the liquid portion of the waste, after filtration, is defined as the TCLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the TCLP extract. For wastes containing >0.5% dry solids (Sections 7.1.1 or 7.1.2), use the percent solids information obtained in Section 7.1.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the TCLP extract.

7.2.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the waste is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.2.7 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder (see Section 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and

subtract it from the sample weight determined in Section 7.2.5, to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within a 2 minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.2.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (See Section 7.2.12) or stored at 4 °C until time of analysis.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Section 7.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.2.9 If the waste contains <0.5% dry solids (see Section 7.1.2), proceed to Section 7.2.13. If the waste contains >0.5% dry solids (see Section 7.1.1 or 7.1.2), and if particle size reduction of the solid was needed in Section 7.1.3, proceed to Section 7.2.10. If the waste as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Section 7.2.11.

7.2.10 Prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described in Section 7.1.3. When the surface area or particle size has been appropriately altered, quantitatively transfer the solid material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon coated sieve should be used to avoid contamination of the sample.

manipulation of these materials should be done when cold (4 °C) to minimize loss of volatiles.

7.3.1 Pre-weigh the (evacuated) filtrate collection container (See Section 4.6) and set aside. If using a TEDLAR® bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis. The containers listed in Section 4.6 are recommended for use under the conditions stated in Sections 4.6.1 - 4.6.3.

7.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Section 7.3, Section 7.1.1 and/or 7.1.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

7.3.3 If the waste is 100% solid (see Section 7.1.1), weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to Section 7.3.5.

7.3.4 If the waste contains < 0.5% dry solids (Section 7.1.2), the liquid portion of waste, after filtration, is defined as the TCLP extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For wastes containing $\geq$ 0.5% dry solids (Sections 7.1.1 and/or 7.1.2), use the percent solids information obtained in Section 7.1.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows:

7.3.4.1 For wastes containing < 5% solids (see Section 7.1.1), weigh out a 500 gram subsample of waste and record the weight.

7.3.4.2 For wastes containing $\geq$ 5% solids (see Section 7.1.1), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{percent solids (Section 7.1.1)}} \times 100$$

Weigh out a subsample of the waste of the appropriate size and record the weight.

7.3.5 If particle size reduction of the solid portion of the waste was required in Section 7.1.3, proceed to Section 7.3.6. If

particle size reduction was not required in Section 7.1.3, proceed to Section 7.3.7.

7.3.6 Prepare the waste for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle size as described in Section 7.1.3. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4 °C prior to particle size reduction. The means used to effect particle size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle size has been appropriately altered, proceed to Section 7.3.7.

7.3.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

7.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Section 7.3.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100% solid (see Section 7.1.1), slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to Section 7.3.12.

7.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Section 7.1.1)} \times \text{weight of waste filtered (Section 7.2.5 or 7.2.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Section 7.1.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ± 2 °C during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

7.2.12 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Section 7.2.7. For final filtration of the TCLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed (see Section 4.4) if evaluating the mobility of metals.

7.2.13 Prepare the TCLP extract as follows:

7.2.13.1 If the waste contained no initial liquid phase, the filtered liquid material obtained from Section 7.2.12 is defined as the TCLP extract. Proceed to Section 7.2.14.

7.2.13.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from Section 7.2.12 with the initial liquid phase of the waste obtained in Section 7.2.7. This combined liquid is defined as the TCLP extract. Proceed to Section 7.2.14.

7.2.13.3 If the initial liquid phase of the waste, as obtained from Section 7.2.7, is not or may not be compatible with the filtered liquid resulting from Section 7.2.12, do not combine these liquids. Analyze these liquids, collectively defined as the TCLP extract, and combine the results mathematically, as described in Section 7.2.14.

7.2.14 Following collection of the TCLP extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to

pH <2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4 °C) until analyzed. The TCLP extract shall be prepared and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to $\pm$ 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)\ (C_1) + (V_2)\ (C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.2.15 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

7.3 Procedure When Volatiles are Involved

Use the ZHE device to obtain TCLP extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of nonvolatile analytes (e.g., metals, pesticides, etc.).

The ZHE device has approximately a 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a sample from which no additional liquid may be forced out by an applied pressure of 50 psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any

7.3.9 Attach the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2 minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.3.10 The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the TCLP extraction as a solid.

If the original waste contained <0.5% dry solids (see Section 7.1.2), this filtrate is defined as the TCLP extract and is analyzed directly. Proceed to Section 7.3.15.

7.3.11 The liquid phase may now be either analyzed immediately (See Sections 7.3.13 through 7.3.15) or stored at 4 °C under minimal headspace conditions until time of analysis. Determine the weight of extraction fluid #1 to add to the ZHE as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Section 7.1.1)} \times \text{weight of waste filtered (Section 7.3.4 or 7.3.8)}}{100}$$

7.3.12 The following Sections detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #1 is used in all cases (See Section 5.7).

7.3.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve,

and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

7.3.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all ZHE fittings to ensure that they are closed.

7.3.12.3 Place the ZHE in the rotary agitation apparatus (if it is not already there) and rotate at 30 $\pm$ 2 rpm for 18 $\pm$ 2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 23 $\pm$ 2 °C during agitation.

7.3.13 Following the 18 $\pm$ 2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the device is leaking. Check the ZHE for leaking as specified in Section 4.2.1, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Section 7.3.9. All extract shall be filtered and collected if the TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (see Sections 4.6 and 7.3.1).

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

7.3.14 If the original waste contained no initial liquid phase, the filtered liquid material obtained from Section 7.3.13 is defined as the TCLP extract. If the waste contained an initial liquid phase, the

filtered liquid material obtained from Section 7.3.13 and the initial liquid phase (Section 7.3.9) are collectively defined as the TCLP extract.

7.3.15 Following collection of the TCLP extract, immediately prepare the extract for analysis and store with minimal headspace at 4 °C until analyzed. Analyze the TCLP extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)\ (C_1) + (V_2)\ (C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phases (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.3.16 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

8.0 QUALITY ASSURANCE

8.1 A minimum of one blank (using the same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in an extraction vessel.

8.2 A matrix spike shall be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data are being used solely to demonstrate that the waste property exceeds the regulatory level. A minimum of one matrix spike must be analyzed for each analytical batch. As a minimum, follow the matrix spike addition guidance provided in each analytical method.

8.2.1 Matrix spikes are to be added after filtration of the TCLP extract and before preservation. Matrix spikes should not be added prior to TCLP extraction of the sample.

8.2.2 In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration, but may not be not less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be

added to the same nominal volume of TCLP extract as that which was analyzed for the unspiked sample.

8.2.3 The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist. Use of other internal calibration methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the analyte concentration in the TCLP extract when the recovery of the matrix spike is below the expected analytical method performance.

8.2.4 Matrix spike recoveries are calculated by the following formula:

$$\%R\ (\%Recovery) = 100\ (X_s - X_u)/K$$

where:
X_s = measured value for the spiked sample,
X_u = measured value for the unspiked sample, and
K = known value of the spike in the sample.

8.3 All quality control measures described in the appropriate analytical methods shall be followed.

8.4 The use of internal calibration quantitation methods shall be employed for a metallic contaminant if: (1) Recovery of the contaminant from the TCLP extract is not at least 50% and the concentration does not exceed the regulatory level, and (2) The concentration of the contaminant measured in the extract is within 20% of the appropriate regulatory level.

8.4.1. The method of standard additions shall be employed as the internal calibration quantitation method for each metallic contaminant.

8.4.2 The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution. It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots. The forth aliquot is the unknown. Preferably, the first addition should be prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100% and 150% of the expected concentration of the sample. All four aliquots are maintained at the same final volume by adding reagent water or a blank solution, and may need dilution adjustment to maintain the signals in the linear range of the instrument technique. All four aliquots are analyzed.

8.4.3 Prepare a plot, or subject data to linear regression, of instrument signals or external-calibration-derived concentrations as the dependant variable (y-axis) versus concentrations of the additions of standard as the independent variable (x-axis). Solve for the intercept of

the abscissa (the independent variable, x-axis) which is the concentration in the unknown.

8.4.4 Alternately, subtract the instrumental signal or external-calibration-derived concentration of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions. Plot or subject to linear regression of the corrected instrument signals or external-calibration-derived concentrations as the dependant variable versus the independent variable. Derive concentrations for unknowns using the internal calibration curve as if it were an external calibration curve.

8.5 Samples must undergo TCLP extraction within the following time periods:

SAMPLE MAXIMUM HOLDING TIMES [Days]				
	From: Field collection To: TCLP extraction	From: TCLP extraction To: Preparative extraction	From: Preparative extraction To: Determinative analysis	Total elapsed time
Volatiles	14	NA	14	28
Semi-volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360

NA = Not applicable

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

9.0 METHOD PERFORMANCE

9.1 Ruggedness. Two ruggedness studies have been performed to determine the effect of various perturbations on specific elements of the TCLP protocol. Ruggedness testing determines the sensitivity of small procedural variations which might be expected to occur during routine laboratory application.

9.1.1 Metals - The following conditions were used when leaching a waste for metals analysis:

Varying Conditions	
Liquid/Solid ratio	19:1 vs. 21:1
Extraction time	16 hours vs. 18 hours
Headspace	20% vs. 60%
Buffer #2 acidity	190 meq vs. 210 meq
Acid-washed filters	yes vs. no
Filter type	0.7 μm glass fiber vs. 0.45 μm vs. polycarbonate
Bottle type	borosilicate vs. flint glass

Of the seven method variations examined, acidity of the extraction fluid had the greatest impact on the results. Four of 13 metals from an API separator sludge/electroplating waste (API/EW) mixture and two of three metals from an ammonia lime still bottom waste were extracted at higher levels by the more acidic buffer. Because of the sensitivity to pH changes, the method requires that the extraction fluids be prepared so that the final pH is within ± 0.05 units as specified.

9.1.2 Volatile Organic Compounds - The following conditions were used when leaching a waste for VOC analysis:

Varying Conditions	
Liquid/Solid ratio	19:1 vs. 21:1
Headspace	0% vs. 5%
Buffer #1 acidity	60 meq vs. 80 meq
Method of storing extract	Syringe vs. Tedlar® bag
Aliquotting	yes vs. no
Pressure behind piston	0 psi vs. 20 psi

None of the parameters had a significant effect on the results of the ruggedness test.

9.2 Precision. Many TCLP precision (reproducibility) studies have been performed, and have shown that, in general, the precision of the TCLP is comparable to or exceeds that of the EP toxicity test and that method precision is adequate. One of the more significant contributions to poor precision appears to be related to sample homogeneity and inter-laboratory variation (due to the nature of waste materials).

9.2.1 Metals - The results of a multi-laboratory study are shown in Table 6, and indicate that a single analysis of a waste may not be adequate for waste characterization and identification requirements.

9.2.2 Semi-Volatile Organic Compounds - The results of two studies are shown in Tables 7 and 8. Single laboratory precision was excellent with greater than 90 percent of the results exhibiting an RSD less than 25 percent. Over 85 percent of all individual compounds in the multi-laboratory study fell in the RSD range of 20 - 120 percent. Both studies concluded that the TCLP provides adequate precision. It was also determined that the high acetate content of the extraction fluid did not present problems (i.e., column degradation of the gas chromatograph) for the analytical conditions used.

9.2.3 Volatile Organic Compounds - Eleven laboratories participated in a collaborative study of the use of the ZHE with two waste types which were fortified with a mixture of VOCs. The results of the collaborative study are shown in Table 9. Precision results for VOCs tend to occur over a considerable range. However, the range and mean RSD compared very closely to the same collaborative study metals results in Table 6. Blackburn and Show concluded that at the 95% level of significance: 1) recoveries among laboratories were statistically similar, 2) recoveries did not vary significantly between the two sample types, and 3) each laboratory showed the same pattern of recovery for each of the two samples.

10.0 REFERENCES

1. Blackburn, W.B. and Show, I. "Collaborative Study of the Toxicity Characteristics Leaching Procedure (TCLP)." Draft Final Report, Contract No. 68-03-1958, S-Cubed, November 1986.

2. Newcomer, L.R., Blackburn, W.B., Kimmell, T.A. "Performance of the Toxicity Characteristic Leaching Procedure." Wilson Laboratories, S-Cubed, U.S. EPA, December 1986.

3. Williams, L.R., Francis, C.W.; Maskarinec, M.P., Taylor D.R., and Rothman, N. "Single-Laboratory Evaluation of Mobility Procedure for Solid Waste." EMSL, ORNL, S-Cubed, ENSECO.

Table 1.
Volatile Analytes[1,2]

Compound	CAS No.
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1,-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[1] When testing for any or all of these analytes, the zero-headspace extractor vessel shall be used instead of the bottle extractor.

[2] Benzene, carbon tetrachloride, chlorobenzene, chloroform, 1,2-dichloroethane, 1,1-dichloroethylene, methyl ethyl ketone, tetrachloroethylene, and vinyl chloride are toxicity characteristic constituents.

Table 2.
Suitable Rotary Agitation Apparatus[1]

Company	Location	Model No.
Analytical Testing and Consulting Services, Inc.	Warrington, PA (215) 343-4490	4-vessel extractor (DC20S) 8-vessel extractor (DC20) 12-vessel extractor (DC20B) 24-vessel extractor (DC24C)
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	2-vessel (3740-2-BRE) 4-vessel (3740-4-BRE) 6-vessel (3740-6-BRE) 8-vessel (3740-8-BRE) 12-vessel (3740-12-BRE) 24-vessel (3740-24-BRE)
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	8-vessel (08-00-00) 4-vessel (04-00-00)
IRA Machine Shop and Laboratory	Santurce, PR (809) 752-4004	8-vessel (011001)
Lars Lande Manufacturing	Whitmore Lake, MI (313) 449-4116	10-vessel (10VRE) 5-vessel (5VRE) 6-vessel (6VRE)
Millipore Corp.	Bedford, MA (800) 225-3384	4-ZHE or 4 2-liter bottle extractor (YT310RAHW)

[1] Any device that rotates the extraction vessel in an end-over-end fashion at 30 ± 2 rpm is acceptable.

Table 3.
Suitable Zero-Headspace Extractor Vessels[1]

Company	Location	Model No.
Analytical Testing & Consulting Services, Inc.	Warrington, PA (215) 343-4490	C102, Mechanical Pressure Device
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	3745-ZHE, Gas Pressure Device
Lars Lande Manufacturing[2]	Whitmore Lake, MI (313) 449-4116	ZHE-11, Gas Pressure Device
Millipore Corporation	Bedford, MA (800) 225-3384	YT30090HW, Gas Pressure Device
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	VOLA-TOX1, Gas Pressure Device
Gelman Science	Ann Arbor, MI (800) 521-1520	15400 Gas Pressure Device

[1] Any device that meets the specifications listed in Section 4.2.1 of the method is suitable.

[2] This device uses a 110 mm filter.

Table 4.
Suitable Filter Holders[1]

Company	Location	Model/ Catalogue No.	Size
Nucleopore Corporation	Pleasanton, CA (800) 882-7711	425910 410400	142 mm 47 mm
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	302400 311400	142 mm 47 mm
Millipore Corporation	Bedford, MA (800) 225-3384	YT30142HW XX1004700	142 mm 47 mm

[1] Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic analytes are of concern. The 142 mm size filter holder is recommended.

Table 5.
Suitable Filter Media[1]

Company	Location	Model	Pore Size (μm)
Millipore Corporation	Bedford, MA (800) 225-3384	AP40	0.7
Nucleopore Corporation	Pleasanton, CA (415) 463-2530	211625	0.7
Whatman Laboratory Products, Inc.	Clifton, NJ (201) 773-5800	GFF	0.7
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	GF75	0.7
Gelman Science	Ann Arbor, MI (800) 521-1520	66256 (90mm) 66257 (142mm)	0.7

[1] Any filter that meets the specifications in Section 4.4 of the Method is suitable.

Table 6. Multi-Laboratory TCLP Metals, Precision

Waste	Extraction Fluid	Metal	$\bar{X}$	S	%RSD
Ammonia	#1	Cadmium	0.053	0.031	60
Lime Still	#2		0.023	0.017	76
Bottoms	#1	Chromium	0.015	0.0014	93
	#2		0.0032	0.0037	118
	#1	Lead	0.0030	0.0027	90
	#2		0.0032	0.0028	87
API/EW	#1	Cadmium	0.0046	0.0028	61
Mixture	#2		0.0005	0.0004	77
	#1	Chromium	0.0561	0.0227	40
	#2		0.105	0.018	17
	#1	Lead	0.0031	0.0031	100
	#2		0.0124	0.0136	110
Fossil	#1	Cadmium	0.080	0.069	86
Fuel Fly	#2		0.093	0.067	72
Ash	#1	Chromium	0.017	0.014	85
	#2		0.070	0.040	57
	#1	Lead	0.0087	0.0074	85
	#2		0.0457	0.0083	18
				%RSD Range = 17 - 118	
				Mean %RSD = 74	

NOTE: $\bar{X}$ = Mean results from 6 - 12 different laboratories
Units = mg/L
Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

Table 7. Single-Laboratory Semi-Volatiles, Precision

Waste	Compound	Extraction Fluid	$\bar{X}$	S	%RSD
Ammonia Lime Still Bottoms	Phenol	#1	19000	2230	11.6
		#2	19400	929	4.8
	2-Methylphenol	#1	2000	297	14.9
		#2	1860	52.9	2.8
	4-Methylphenol	#1	7940	1380	17.4
		#2	7490	200	2.7
	2,4-Dimethylphenol	#1	321	46.8	14.6
		#2	307	45.8	14.9
	Naphthalene	#1	3920	413	10.5
		#2	3827	176	4.6
	2-Methylnaphthalene	#1	290	44.8	15.5
		#2	273	19.3	7.1
	Dibenzofuran	#1	187	22.7	12.1
		#2	187	7.2	3.9
	Acenaphthylene	#1	703	89.2	12.7
		#2	663	20.1	3.0
	Fluorene	#1	151	17.6	11.7
		#2	156	2.1	1.3
	Phenanthrene	#1	241	22.7	9.4
		#2	243	7.9	3.3
	Anthracene	#1	33.2	6.19	18.6
		#2	34.6	1.55	4.5
	Fluoranthrene	#1	25.3	1.8	7.1
		#2	26.0	1.8	7.1
API/EW Mixture	Phenol	#1	40.7	13.5	33.0
		#2	19.0	1.76	9.3
	2,4-Dimethylphenol	#1	33.0	9.35	28.3
		#2	43.3	8.61	19.9
	Naphthalene	#1	185	29.4	15.8
		#2	165	24.8	15.0
	2-Methylnaphthalene	#1	265	61.2	23.1
		#2	200	18.9	9.5
				%RSD Range = 1 - 33	
				Mean %RSD = 12	

NOTE: Units = μg/L
Extractions were performed in triplicate
All results were at least 2x the detection limit
Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

Table 8. Multi-Laboratory Semi-Volatiles, Precision

Waste	Compound	Extraction Fluid	$\bar{X}$	S	%RSD
Ammonia Lime	BNAs	#1	10043	7680	76.5
Still Bottoms (A)		#2	10376	6552	63.1
API/EW	BNAs	#1	1624	675	41.6
Mixture (B)		#2	2074	1463	70.5
Fossil Fuel	BNAs	#1	750	175	23.4
Fly Ash (C)		#2	739	342	46.3
					Mean %RSD = 54

NOTE: Units = µg/L
$\bar{X}$ = Mean results from 3 - 10 labs
Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

%RSD Range for Individual Compounds

A, #1	0 - 113
A, #2	28 - 108
B, #1	20 - 156
B, #2	49 - 128
C, #1	36 - 143
C, #2	61 - 164

Table 9. Multi-Laboratory (11 Labs) VOCs, Precision

Waste	Compound	$\bar{X}$	S	%RSD
Mine Tailings	Vinyl chloride	6.36	6.36	100
	Methylene chloride	12.1	11.8	98
	Carbon disulfide	5.57	2.83	51
	1,1-Dichloroethene	21.9	27.7	127
	1,1-Dichloroethane	31.4	25.4	81
	Chloroform	46.6	29.2	63
	1,2-Dichloroethane	47.8	33.6	70
	2-Butanone	43.5	36.9	85
	1,1,1-Trichloroethane	20.9	20.9	100
	Carbon tetrachloride	12.0	8.2	68
	Trichloroethene	24.7	21.2	86
	1,1,2-Trichloroethene	19.6	10.9	56
	Benzene	37.9	28.7	76
	1,1,2,2-Tetrachloroethane	34.9	25.6	73
	Toluene	29.3	11.2	38
	Chlorobenzene	35.6	19.3	54
	Ethylbenzene	4.27	2.80	66
	Trichlorofluoromethane	3.82	4.40	115
	Acrylonitrile	76.7	110.8	144
Ammonia Lime Still Bottoms	Vinyl chloride	5.00	4.71	94
	Methylene chloride	14.3	13.1	92
	Carbon disulfide	3.37	2.07	61
	1,1-Dichloroethene	52.1	38.8	75
	1,1-Dichloroethane	52.8	25.6	49
	Chloroform	64.7	28.4	44
	1,2-Dichloroethane	43.1	31.5	73
	2-Butanone	59.0	39.6	67
	1,1,1-Trichloroethane	53.6	40.9	76
	Carbon tetrachloride	7.10	6.1	86
	Trichloroethene	57.3	34.2	60
	1,1,2-Trichloroethene	6.7	4.7	70
	Benzene	61.3	26.8	44
	1,1,2,2-Tetrachloroethane	3.16	2.1	66
	Toluene	69.0	18.5	27
	Chlorobenzene	71.8	12.0	17
	Ethylbenzene	3.70	2.2	58
	Trichlorofluoromethane	4.05	4.8	119
	Acrylonitrile	29.4	34.8	118
			%RSD Range = 17 - 144 Mean %RSD = 75	

NOTE: Units = μg/L

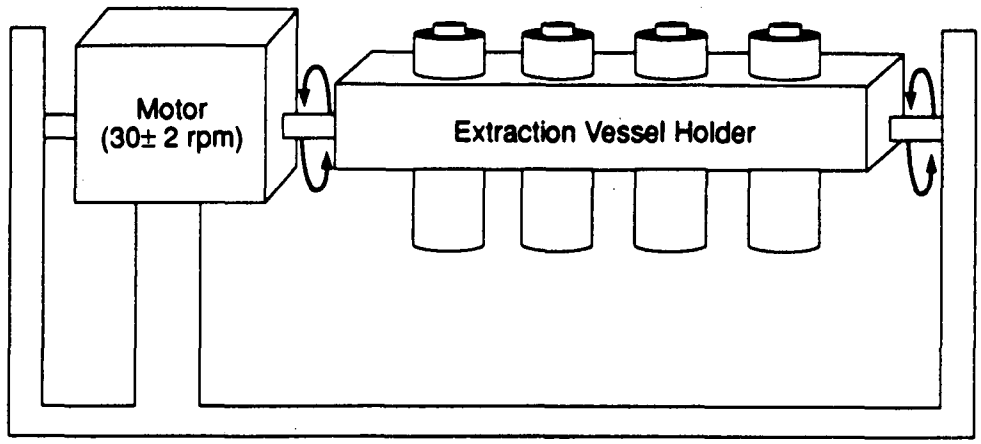


Figure 1. Rotary Agitation Apparatus

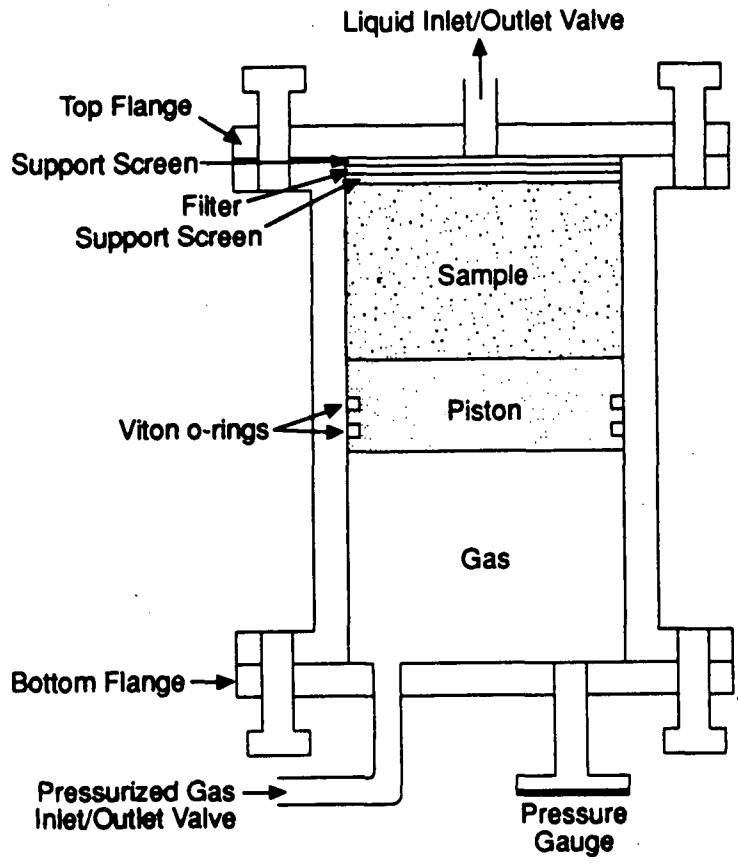
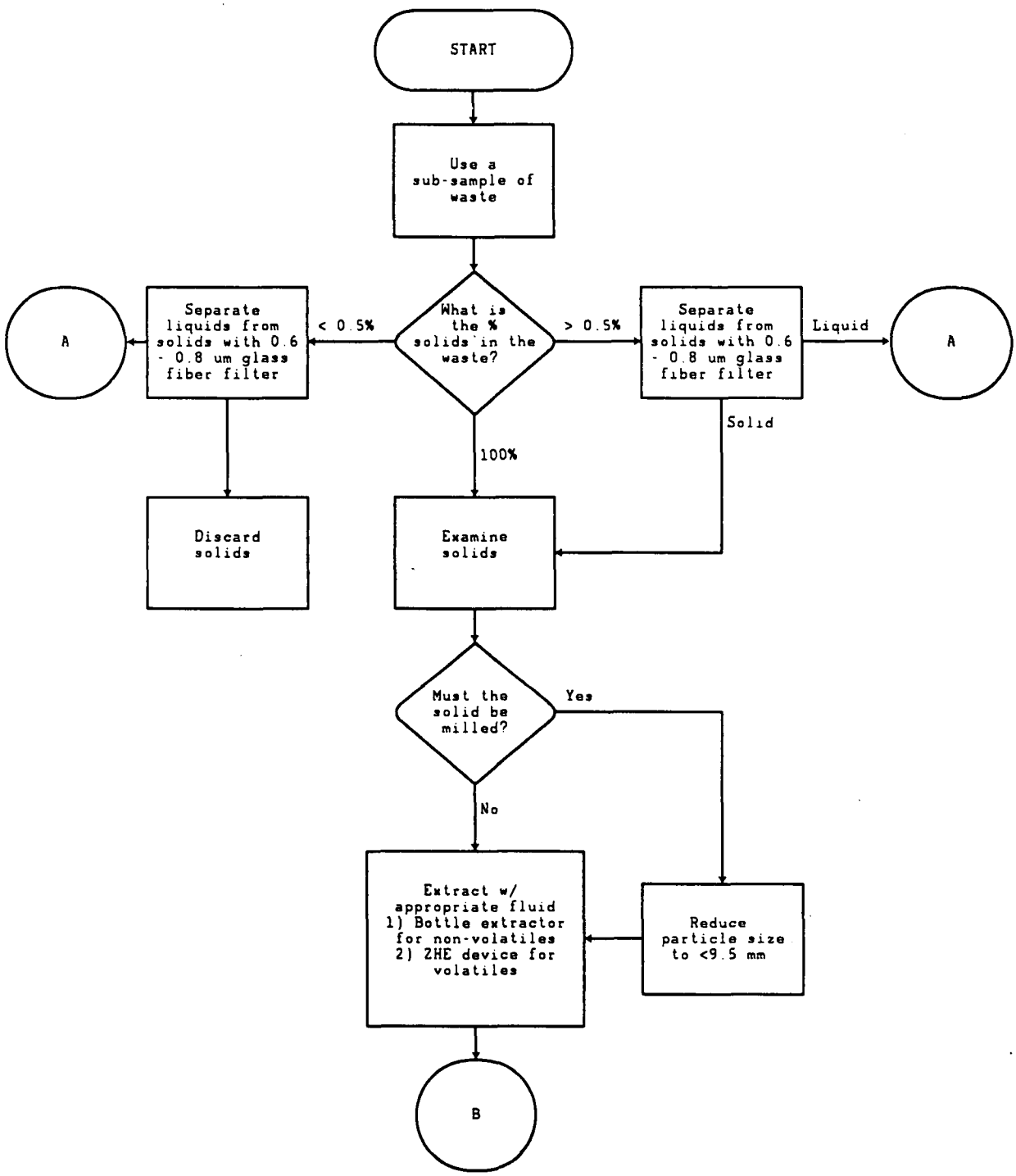


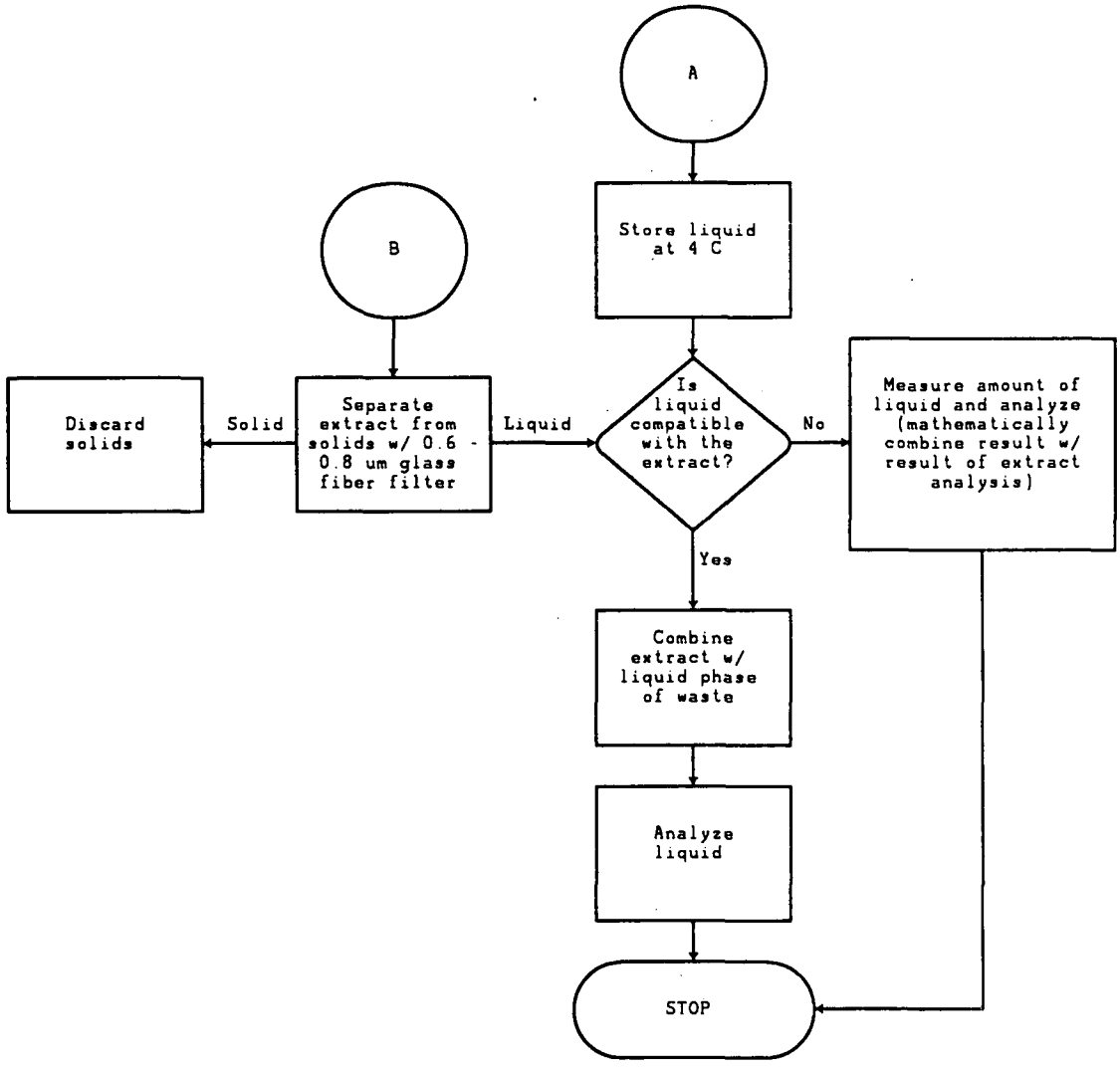
Figure 2. Zero-Headspace Extractor (ZHE)

METHOD 1311

TOXICITY CHARACTERISTIC LEACHATE PROCEDURE



TOXICITY CHARACTERISTIC LEACHATE PROCEDURE



APPENDIX

COMPANY REFERENCES

The following listing of frequently-used addresses is provided for the convenience of users of this manual. No endorsement is intended or implied.

Ace Glass Company
1342 N.W. Boulevard
P.O. Box 688
Vineland, NJ 08360
(609) 692-3333

Aldrich Chemical Company
Department T
P.O. Box 355
Milwaukee, WI 53201

Alpha Products
5570 - T W. 70th Place
Chicago, IL 60638
(312) 586-9810

Barneby and Cheney Company
E. 8th Avenue and N. Cassidy Street
P.O. Box 2526
Columbus, OH 43219
(614) 258-9501

Bio - Rad Laboratories
2200 Wright Avenue
Richmond, CA 94804
(415) 234-4130

Burdick & Jackson Lab Inc.
1953 S. Harvey Street
Muskegon, MO 49442

Calgon Corporation
P.O. Box 717
Pittsburgh, PA 15230
(412) 777-8000

Conostan Division
Conoco Speciality Products, Inc.
P.O. Box 1267
Ponca City, OK 74601
(405) 767-3456

Corning Glass Works
Houghton Park
Corning, NY 14830
(315) 974-9000

Dohrmann, Division of Xertex Corporation
3240 - T Scott Boulevard
Santa Clara, CA 95050
(408) 727-6000
(800) 538-7708

E. M. Laboratories, Inc.
500 Executive Boulevard
Elmsford, NY 10523

Fisher Scientific Co.
203 Fisher Building
Pittsburgh, PA 15219
(412) 562-8300

General Electric Corporation
3135 Easton Turnpike
Fairfield, CT 06431
(203) 373-2211

Graham Manufactory Co., Inc.
20 Florence Avenue
Batavia, NY 14020
(716) 343-2216

Hamilton Industries
1316 18th Street
Two Rivers, WI 54241
(414) 793-1121

ICN Life Sciences Group
3300 Hyland Avenue
Costa Mesa, CA 92626

Johns - Manville Corporation
P.O. Box 5108
Denver, CO 80217

Kontes Glass Company
8000 Spruce Street
Vineland, NJ 08360

Millipore Corporation
80 Ashby Road
Bedford, MA 01730
(617) 275-9200
(800) 225-1380

National Bureau of Standards
U.S. Department of Commerce
Washington, DC 20234
(202) 921-1000

Pierce Chemical Company
Box 117
Rockford, IL 61105
(815) 968-0747

Scientific Glass and Instrument, Inc.
7246 - T Wynnwood
P.O. Box 6
Houston, TX 77001
(713) 868-1481

Scientific Products Company
1430 Waukegon Road
McGaw Park, IL 60085
(312) 689-8410

Spex Industries
3880 - T and Park Avenue
Edison, NJ 08820

Waters Associates
34 - T Maple Street
Milford, MA 01757
(617) 478-2000
(800) 252-4752

Whatman Laboratory Products, Inc.
Clifton, NJ 07015
(201) 773-5800

Revision 0
Date September 1986

☆ U. S. GOVERNMENT PRINTING OFFICE : 1986 O - 169-934

United States
Environmental Protection
Agency

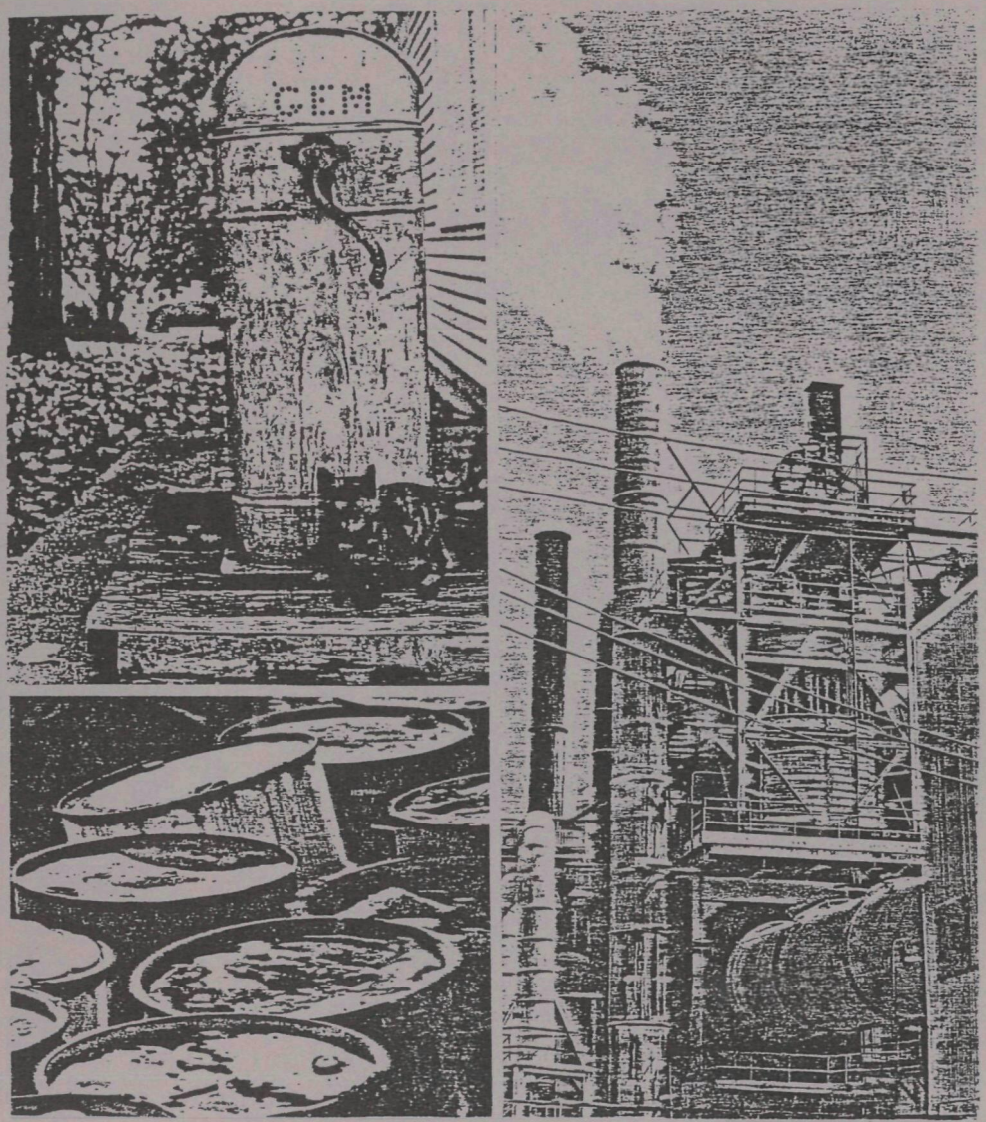
Office of Solid Waste
and Emergency Response
Washington, DC 20460

November 1986
SW-846
Third Edition

Solid Waste

Test Methods for Evaluating Solid Waste

Volume II: Field Manual
Physical / Chemical Methods



Test Methods for Evaluating Solid Waste Physical/Chemical Methods

Third Edition

Proposed Update Package

Instructions

Enclosed is the proposed Update I package for "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," SW-846, Third Edition. Attached is a list of methods included in the proposed update indicating whether the method is a new method, a partially revised method, or a totally revised method.

Do not discard or replace any of the current pages in the SW-846 manual until the proposed Update I package is promulgated. Until promulgation of the update package, the methods in the update package are not officially part of the SW-846 manual and thus do not carry the status of EPA approved methods.

In addition to the proposed Update I package, six finalized methods are included for immediate inclusion into the Third Edition of SW-846. Four methods, originally proposed October 1, 1984, will be finalized in a soon to be released rulemaking. They are, however, being submitted to subscribers for the first time in this update. These methods are 7211, 7381, 7461 and 7951. Two other methods were finalized in the Second Edition of SW-846. They were inadvertantly omitted from the Third Edition and are not being proposed as new. These methods are 7081 and 7761.

Enclosure

METHODS INCLUDED IN PROPOSED UPDATE PACKAGE I

*	Chapter 1	Definitions
*	Chapter 2	Tables
*	Chapter 4	Table 4-1
*	Chapter 7	Reactive Cyanide and Sulfide
*	Method 1310	Extraction Procedure (EP) Toxicity Test Method and Structural Integrity Test
*	Method 1330	Extraction Procedure for Oily Wastes
*	Method 3005	Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by Flame Atomic Absorption Spectroscopy or Inductively Coupled Plasma Spectroscopy
*	Method 3010	Acid Digestion of Aqueous Samples of Extracts for Total Metals for Analysis by Flame Atomic Absorption Spectroscopy or Inductively Coupled Plasma Spectroscopy
*	Method 3020	Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by Furnace Atomic Absorption Spectroscopy
*	Method 3050	Acid Digestion of Sediments, Sludges, and Soils
*	Method 3510	Separatory Funnel Liquid - Liquid Extraction
*	Method 3520	Continuous Liquid-Liquid Extraction
*	Method 3540	Soxhlet Extraction
*	Method 3600	Cleanup
T	Method 3650	Acid-Base Partition Cleanup
*	Method 5030	Purge-and-Trap
T	Method 6010	Inductively Coupled Plasma Atomic Emission Spectroscopy
*	Method 7000	Atomic Absorption Methods
*	Method 7061	Arsenic (AA, Gaseous Hydride)
N	Method 7081	Barium (AA, Furnace Technique)
*	Method 7196	Chromium, Hexavalent (Colorimetric)
N	Method 7211	Copper (AA, Furnace Technique)
N	Method 7381	Iron (AA, Furnace Technique)
N	Method 7430	Lithium (AA, Direct Aspiration)
N	Method 7461	Manganese (AA, Furnace Technique)
T	Method 7760	Silver (AA, Direct Aspiration)
N	Method 7761	Silver (AA, Furnace Technique)
N	Method 7780	Strontium (AA, Direct Aspiration)
N	Method 7951	Zinc (AA, Furnace Technique)
*	Method 8000	Gas Chromatography
*	Method 8010	Halogenated Volatile Organics
N	Method 8011	1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane in Water by Microextraction and Gas Chromatography
*	Method 8015	Nonhalogenated Volatile Organics
N	Method 8021	Volatile Organic Compounds in Water by Purge-and-Trap Capillary Column Gas Chromatography with PID and Electroconductivity Detector in Series
*	Method 8030	Acrolein, Acrylonitrile, Acetonitrile
*	Method 8040	Phenols
N	Method 8070	Nitrosamines
N	Method 8110	Haloethers
*	Method 8120	Chlorinated Hydrocarbons
N	Method 8141	Organophosphorus Pesticides Capillary Column
*	Method 8150	Chlorinated Herbicides
*	Method 8240	GC/MS for Volatile Organics
*	Method 8250	GC/MS for Semivolatile Organics: Packed Column Technique
N	Method 8260	GC/MS for Volatile Organics: Capillary Column

METHODS INCLUDED IN PROPOSED UPDATE PACKAGE I (cont'd)

* Method 8270 - GC/MS for Semivolatile Organics: Capillary Column Technique
T Method 9010 and 9010A - Total and Amenable Cyanides
N Method 9021 - Purgeable Organic Halides (POX)
T Method 9030 - Acid-Soluble and Acid-Insoluble Sulfides
N Method 9031 - Extractable Sulfides
* Method 9090 - Compatibility Test for Wastes and Membrane Liners

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* Indicates partial revision
N Indicates a new method
T Indicates a total revision

VOLUME TWO

Revision 0
Date September 1986

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402

ABSTRACT

This manual provides test procedures which may be used to evaluate those properties of a solid waste which determine whether the waste is a hazardous waste within the definition of Section 3001 of the Resource Conservation and Recovery Act (PL 94-580). These methods are approved for obtaining data to satisfy the requirement of 40 CFR Part 261, Identification and Listing of Hazardous Waste. This manual encompasses methods for collecting representative samples of solid wastes, and for determining the reactivity, corrosivity, ignitability, and composition of the waste and the mobility of toxic species present in the waste.

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VOLUME ONE,

SECTION A

CHAPTER THREE — METALLIC ANALYTES

VOLUME ONE,

SECTION B

VOLUME ONE,

SECTION C

VOLUME TWO

PART IV MONITORING

METHOD INDEX AND CONVERSION TABLE

Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
0010	Ten	0010	0
0020	Ten	0020	0
0030	Ten	0030	0
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1020	Eight (8.1)	1020	0
1110	Eight (8.2)	1110	0
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9095	Six	9095	0
9100	Six	9100	0
9131	Five	9131	0
9132	Five	9132	0
9200	Five	9200	0
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9252	Five	9252	0
9310	Six	9310	0
9315	Six	9315	0
9320	Five	9320	0
HCN Test Method	Seven	HCN Test Method	0
H_2S Test Method	Seven	H_2S Test Method	0

PURPOSE OF THE MANUAL

Test Methods for Evaluating Solid Waste (SW-846) is intended to provide a unified, up-to-date source of information on sampling and analysis related to compliance with RCRA regulations. It brings together into one reference all sampling and testing methodology approved by the Office of Solid Waste for use in implementing the RCRA regulatory program. The manual provides methodology for collecting and testing representative samples of waste and other materials to be monitored. Aspects of sampling and testing covered in SW-846 include quality control, sampling plan development and implementation, analysis of inorganic and organic constituents, the estimation of intrinsic physical properties, and the appraisal of waste characteristics.

The procedures described in this manual are meant to be comprehensive and detailed, coupled with the realization that the problems encountered in sampling and analytical situations require a certain amount of flexibility. The solutions to these problems will depend, in part, on the skill, training, and experience of the analyst. For some situations, it is possible to use this manual in rote fashion. In other situations, it will require a combination of technical abilities, using the manual as guidance rather than in a step-by-step, word-by-word fashion. Although this puts an extra burden on the user, it is unavoidable because of the variety of sampling and analytical conditions found with hazardous wastes.

ORGANIZATION AND FORMAT

This manual is divided into two volumes. Volume I focuses on laboratory activities and is divided for convenience into three sections. Volume IA deals with quality control, selection of appropriate test methods, and analytical methods for metallic species. Volume IB consists of methods for organic analytes. Volume IC includes a variety of test methods for miscellaneous analytes and properties for use in evaluating the waste characteristics. Volume II deals with sample acquisition and includes quality control, sampling plan design and implementation, and field sampling methods. Included for the convenience of sampling personnel are discusssions of the ground water, land treatment, and incineration monitoring regulations.

Volume I begins with an overview of the quality control precedures to be imposed upon the sampling and analytical methods. The quality control chapter (Chapter One) and the methods chapters are interdependent. The analytical procedures cannot be used without a thorough understanding of the quality control requirements and the means to implement them. This understanding can be achieved only be reviewing Chapter One and the analytical methods together. It is expected that individual laboratories, using SW-846 as the reference

source, will select appropriate methods and develop a standard operating procedure (SOP) to be followed by the laboratory. The SOP should incorporate the pertinent information from this manual adopted to the specific needs and circumstances of the individual laboratory as well as to the materials to be evaluated.

The method selection chapter (Chapter Two) presents a comprehensive discussion of the application of these methods to various matrices in the determination of groups of analytes or specific analytes. It aids the chemist in constructing the correct analytical method from the array of procedures which may cover the matrix/analyte/concentration combination of interests. The section discusses the objective of the testing program and its relationship to the choice of an analytical method. Flow charts are presented along with tables to guide in the selection of the correct analytical procedures to form the appropriate method.

The analytical methods are separated into distinct procedures describing specific, independent analytical operations. These include extraction, digestion, cleanup, and determination. This format allows linking of the various steps in the analysis according to: the type of sample (e.g., water, soil, sludge, still bottom); analytes(s) of interest; needed sensitivity; and available analytical instrumentation. The chapters describing Miscellaneous Test Methods and Properties, however, give complete methods which are not amenable to such segmentation to form discrete procedures.

The introductory material at the beginning of each section containing analytical procedures presents information on sample handling and preservation, safety, and sample preparation.

Part II of Volume I (Chapters Seven and Eight) describes the characteristics of a waste. Sections following the regulatory descriptions contain the methods used to determine if the waste is hazardous because it exhibits a particular characteristic.

Volume II gives background information on statistical and nonstatistical aspects of sampling. It also presents practical sampling techniques appropriate for situations presenting a variety of physical conditions.

A discussion of the regulatory requirements with respect to several monitoring categories is also given in this volume. These include ground water monitoring, land treatment, and incineration. The purpose of this guidance is to orient the user to the objective of the analysis, and to assist in developing data quality objectives, sampling plans, and laboratory SOP's.

Significant interferences, or other problems, may be encountered with certain samples. In these situations, the analyst is advised to contact the Chief, Methods Section (WH-562B) Technical Assessment Branch, Office of Solid Waste, US EPA, Washington, DC 20460 (202-382-4761) for assistance. The manual is intended to serve all those with a need to evaluate solid waste. Your comments, corrections, suggestions, and questions concerning any material contained in, or omitted from, this manual will be gratefully appreciated. Please direct your comments to the above address.

CHAPTER ONE,
REPRINTED

QUALITY CONTROL

1.1 INTRODUCTION

Appropriate use of data generated under the great range of analytical conditions encountered in RCRA analyses requires reliance on the quality control practices incorporated into the methods and procedures. The Environmental Protection Agency generally requires using approved methods for sampling and analysis operations fulfilling regulatory requirements, but the mere approval of these methods does not guarantee adequate results. Inaccuracies can result from many causes, including unanticipated matrix effects, equipment malfunctions, and operator error. Therefore, the quality control component of each method is indispensable.

The data acquired from quality control procedures are used to estimate and evaluate the information content of analytical data and to determine the necessity or the effect of corrective action procedures. The means used to estimate information content include precision, accuracy, detection limit, and other quantifiable and qualitative indicators.

1.1.1 Purpose of this Chapter

This chapter defines the quality control procedures and components that are mandatory in the performance of analyses, and indicates the quality control information which must be generated with the analytical data. Certain activities in an integrated program to generate quality data can be classified as management (QA) and other as functional (QC). The presentation given here is an overview of such a program.

The following sections discuss some minimum standards for QA/QC programs. The chapter is not a guide to constructing quality assurance project plans, quality control programs, or a quality assurance organization. Generators who are choosing contractors to perform sampling or analytical work, however, should make their choice only after evaluating the contractor's QA/QC program against the procedures presented in these sections. Likewise, laboratories that sample and/or analyze solid wastes should similarily evaluate their QA/QC programs.

Most of the laboratories who will use this manual also carry out testing other than that called for in SW-846. Indeed, many user laboratories have multiple mandates, including analyses of drinking water, wastewater, air and industrial hygiene samples, and process samples. These laboratories will, in most cases, already operate under an organizational structure that includes QA/QC. Regardless of the extent and history of their programs, the users of this manual should consider the development, status, and effectiveness of their QA/QC program in carrying out the testing described here.

1.1.2 Program Design

The initial step for any sampling or analytical work should be strictly to define the program goals. Once the goals have been defined, a program must be designed to meet them. QA and QC measures will be used to monitor the program and to ensure that all data generated are suitable for their intended use. The responsibility of ensuring that the QA/QC measures are properly employed must be assigned to a knowledgeable person who is not directly involved in the sampling or analysis.

One approach that has been found to provide a useful structure for a QA/QC program is the preparation of both general program plans and project-specific QA/QC plans.

The program plan for a laboratory sets up basic laboratory policies, including QA/QC, and may include standard operating procedures for specific tests. The program plan serves as an operational charter for the laboratory, defining its purposes, its organization and its operating principles. Thus, it is an orderly assemblage of management policies, objectives, principles, and general procedures describing how an agency or laboratory intends to produce data of known and accepted quality. The elements of a program plan and its preparation are described in QAMS-004/80.

Project-specific QA/QC plans differ from program plans in that specific details of a particular sampling/analysis program are addressed. For example, a program plan might state that all analyzers will be calibrated according to a specific protocol given in written standard operating procedures for the laboratory (SOP), while a project plan would state that a particular protocol will be used to calibrate the analyzer for a specific set of analyses that have been defined in the plan. The project plan draws on the program plan or its basic structure and applies this management approach to specific determinations. A given agency or laboratory would have only one quality assurance program plan, but would have a quality assurance project plan for each of its projects. The elements of a project plan and its preparation are described in QAMS/005/80 and are listed in Figure 1-1.

Some organizations may find it inconvenient or even unnecessary to prepare a new project plan for each new set of analyses, especially analytical laboratories which receive numerous batches of samples from various customers within and outside their organizations. For these organizations, it is especially important that adequate QA management structures exist and that any procedures used exist as standard operating procedures (SOP), written documents which detail an operation, analysis or action whose mechanisms are thoroughly prescribed and which is commonly accepted as the method for performing certain routine or repetitive tasks. Having copies of SW-846 and all its referenced documents in one's laboratory is not a substitute for having in-house versions of the methods written to conform to specific instrumentation, data needs, and data quality requirements.

FIGURE 1-1

ESSENTIAL ELEMENTS OF A QA PROJECT PLAN

1. Title Page
2. Table of Contents
3. Project Description
4. Project Organization and Responsibility
5. QA Objectives
6. Sampling Procedures
7. Sample Custody
8. Calibration Procedures and Frequency
9. Analytical Procedures
10. Data Reduction, Validation, and Reporting
11. Internal Quality Control Checks
12. Performance and System Audits
13. Preventive Maintenance
14. Specific Routine Procedures Used to Assess Data Precision, Accuracy, and Completeness
15. Corrective Action
16. Quality Assurance Reports to Management

1.1.3 Organization and Responsibility

As part of any measurement program, activities for the data generators, data reviewers/approvers, and data users/requestors must be clearly defined. While the specific titles of these individuals will vary among agencies and laboratories, the most basic structure will include at least one representative of each of these three types. The data generator is typically the individual who carries out the analyses at the direction of the data user/requestor or a designate within or outside the laboratory. The data reviewer/approver is responsible for ensuring that the data produced by the data generator meet agreed-upon specifications.

Responsibility for data review is sometimes assigned to a "Quality Assurance Officer" or "QA Manager." This individual has broad authority to approve or disapprove project plans, specific analyses and final reports. The QA Officer is independent from the data generation activities. In general, the QA Officer is responsible for reviewing and advising on all aspects of QA/QC, including:

Assisting the data requestor in specifying the QA/QC procedure to be used during the program;

Making on-site evaluations and submitting audit samples to assist in reviewing QA/QC procedures; and,

f problems are detected, making recommendations to the data requestor and upper corporate/institutional management to ensure that appropriate corrective actions are taken.

In programs where large and complex amounts of data are generated from both field and laboratory activities, it is helpful to designate sampling monitors, analysis monitors, and quality control/data monitors to assist in carrying out the program or project.

The sampling monitor is responsible for field activities. These include:

Determining (with the analysis monitor) appropriate sampling equipment and sample containers to minimize contamination;

Ensuring that samples are collected, preserved, and transported as specified in the workplan; and

Checking that all sample documentation (labels, field notebooks, chain-of-custody records, packing lists) is correct and transmitting that information, along with the samples, to the analytical laboratory.

The analysis monitor is responsible for laboratory activities. These include:

Training and qualifying personnel in specified laboratory QC and analytical procedures, prior to receiving samples;

Receiving samples from the field and verifying that incoming samples correspond to the packing list or chain-of-custody sheet; and

Verifying that laboratory QC and analytical procedures are being followed as specified in the workplan, reviewing sample and QC data during the course of analyses, and, if questionable data exist, determining which repeat samples or analyses are needed.

The quality control and data monitor is responsible for QC activities and data management. These include:

Maintaining records of all incoming samples, tracking those samples through subsequent processing and analysis, and, ultimately, appropriately disposing of those samples at the conclusion of the program;

Preparing quality control samples for analysis prior to and during the program;

Preparing QC and sample data for review by the analysis coordinator and the program manager; and

Preparing QC and sample data for transmission and entry into a computer data base, if appropriate.

1.1.4 Performance and Systems Audits

The QA Officer may carry out performance and/or systems audits to ensure that data of known and defensible quality are produced during a program,.

Systems audits are qualitative evaluations of all components of field and laboratory quality control measurement systems. They determine if the measurement systems are being used appropriately. The audits may be carried out before all systems are operational, during the program, or after the completion of the program. Such audits typically involve a comparison of the activities given in the QA/QC plan with those actually scheduled or performed. A special type of systems audit is the data management audit. This audit addresses only data collection and management activities.

The performance audit is a quantitative evaluation of the measurement systems of a program. It requires testing the measurement systems with samples of known composition or behavior to evaluate precision and accuracy. The performance audit is carried out by or under the auspices of the QA Officer without the knowledge of the analysts. Since this is seldom achievable, many variations are used that increase the awareness of the analyst as to the nature of the audit material.

1.1.5 Corrective Action

Corrective action procedures should be addressed in the program plan, project, or SOP. These should include the following elements:

The EPA predetermined limits for data acceptability beyond which corrective action is required;

Procedures for corrective action; and,

For each measurement system, identification of the individual responsible for initiating the corrective action and the individual responsible for approving the corrective action, if necessary.

The need for corrective action may be identified by system or performance audits or by standard QC procedures. The essential steps in the corrective action system are:

Identification and definition of the problem;

Assignment of responsibility for investigating the problem;

Investigation and determination of the cause of the problem;

Determination of a corrective action to eliminate the problem;

Assigning and accepting responsibility for implementing the corrective action;

Implementing the corrective action and evaluating its effectiveness; and

Verifying that the corrective action has eliminated the problem.

The QA Officer should ensure that these steps are taken and that the problem which led to the corrective action has been resolved.

1.1.6 QA/QC Reporting to Management

QA Project Program or Plans should provide a mechanism for periodic reporting to management (or to the data user) on the performance of the measurement system and the data quality. Minimally, these reports should include:

Periodic assessment of measurement quality indicators, i.e., data accuracy, precision and completeness;

Results of performance audits;

Results of system audits; and

Significant QA problems and recommended solutions.

The individual responsible within the organization structure for preparing the periodic reports should be identified in the organizational or management plan. The final report for each project should also include a separate QA section which summarizes data quality information contained in the periodic reports.

Other guidance on quality assurance management and organizations is available from the Agency and professional organizations such as ASTM, AOAC, APHA and FDA.

1.1.7 Quality Control Program for the Analysis of RCRA Samples

An analytical quality control program develops information which can be used to:

Evaluate the accuracy and precision of analytical data in order to establish the quality of the data;

Provide an indication of the need for corrective actions, when comparison with existing regulatory or program criteria or data trends shows that activities must be changed or monitored to a different degree; and

To determine the effect of corrective actions.

1.1.8 Definitions

ACCURACY: Accuracy means the nearness of a result or the mean ($\bar{X}$) of a set of results to the true value. Accuracy is assessed by means of reference samples and percent recoveries.

ANALYTICAL BATCH: The basic unit for analytical quality control is the analytical batch. The analytical batch is defined as samples which are analyzed together with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar composition.

BLANK: A blank is an artificial sample designed to monitor the introduction of artifacts into the process. For aqueous samples, reagent water is used as a blank matrix; however, a universal blank matrix does not exist for solid samples, and therefore, no matrix is used. The blank is taken through the appropriate steps of the process.
A reagent blank is an aliquot of analyte-free water or solvent analyzed with the analytical batch. Field blanks are aliquots of analyte-free water or solvents brought to the field in sealed containers and transported back to the

laboratory with the sample containers. Trip blanks and equipment blanks are two specific types of field blanks. Trip blanks are not opened in the field. They are a check on sample contamination originating from sample transport, shipping and from site conditions. Equipment blanks are opened in the field and the contents are poured appropriately over or through the sample collection device, collected in a sample container, and returned to the laboratory as a sample. Equipment blanks are a check on sampling device cleanliness.

CALIBRATION CHECK: Verification of the ratio of instrument response to analyte amount, a calibration check, is done by analyzing for analyte standards in an appropriate solvent. Calibration check solutions are made from a stock solution which is different from the stock used to prepare standards.

CHECK SAMPLE: A blank which has been spiked with the analyte(s) from an independent source in order to monitor the execution of the analytical method is called a check sample. The level of the spike shall be at the regulatory action level when applicable. Otherwise, the spike shall be at 5 times the estimate of the quantification limit. The matrix used shall be phase matched with the samples and well characterized: for an example, reagent grade water is appropriate for an aqueous sample.

ENVIRONMENTAL SAMPLE: An environmental sample or field sample is a representative sample of any material (aqueous, nonaqueous, or multimedia) collected from any source for which determination of composition or contamination is requested or required. For the purposes of this manual, environmental samples shall be classified as follows:

Surface Water and Ground Water;

Drinking Water -- delivered (treated or untreated) water designated as potable water;

Water/Wastewater -- raw source waters for public drinking water supplies, ground waters, municipal influents/effluents, and industrial influents/effluents;

Sludge -- municipal sludges and industrial sludges;

Waste -- aqueous and nonaqueous liquid wastes, chemical solids, contaminated soils, and industrial liquid and solid wastes.

MATRIX/SPIKE-DUPLICATE ANALYSIS: In matrix/spike duplicate analysis, predetermined quantities of stock solutions of certain analytes are added to a added to a sample matrix prior to sample extraction/digestion and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected. The relative percent difference between the samples is calculated and used to assess analytical precision. The concentration of the spike should be at the regulatory standard level or the estimated or actual method quantification limit. When the concentration of the analyte in the sample is greater than 0.1%, no spike of the analyte is necessary.

MQL: The method quantification limit (MQL) is the minimum concentration of a substance that can be measured and reported.

PRECISION: Precision means the measurement of agreement of a set of replicate results among themselves without assumption of any prior information as to the true result. Precision is assessed by means of duplicate/replicate sample analysis.

PQL: The practical quantitation limit (PQL) is the lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions.

RCRA: The Resource Conservation and Recovery Act.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonomous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REPLICATE SAMPLE: A replicate sample is a sample prepared by dividing a sample into two or more separate aliquots. Duplicate samples are considered to be two replicates.

STANDARD CURVE: A standard curve is a curve which plots concentrations of known analyte standard versus the instrument response to the analyte.

SURROGATE: Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, standards, samples and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

WATER: Reagent, analyte-free, or laboratory pure water means distilled or deionized water or Type II reagent water which is free of contaminants that may interfere with the analytical test in question.

1.2 QUALITY CONTROL

The procedures indicated below are to be performed for all analyses. Specific instructions relevant to particular analyses are given in the pertinent analytical procedures.

1.2.1 Field Quality Control

The sampling component of the Quality Assurance Project Plan (QAPP) shall include:

Reference to or incorporation of accepted sampling techniques in the sampling plan;

Procedures for documenting and justifying any field actions contrary to the QAPP;

Documentation of all pre-field activities such as equipment check-out, calibrations, and container storage and preparation;

Documentation of field measurement quality control data (quality control procedures for such measurements shall be equivalent to corresponding laboratory QC procedures);

Documentation of field activities;

Documentation of post-field activities including sample shipment and receipt, field team de-briefing and equipment check-in;

Generation of quality control samples including duplicate samples, field blanks, equipment blanks, and trip blanks; and

The use of these samples in the context of data evaluation, with details of the methods employed (including statistical methods) and of the criteria upon which the information generated will be judged.

1.2.2 Analytical Quality Control

A quality control operation or component is only useful if it can be measured or documented. The following components of analytical quality control are related to the analytical batch. The procedures described are intended to be applied to chemical analytical procedures; although the principles are applicable to radio-chemical or biological analysis, the procedures may not be directly applicable to such techniques.

All quality control data and records required by this section shall be retained by the laboratory and shall be made available to the data requestor as appropriate. The frequencies of these procedures shall be as stated below or at least once with each analytical batch.

1.2.2.1 Spikes, Blanks and Duplicates

General Requirements

These procedures shall be performed at least once with each analytical batch with a minimum of once per twenty samples.

1.2.2.1.1 Duplicate Spike

A split/spiked field sample shall be analyzed with every analytical batch or once in twenty samples, whichever is the greater frequency. Analytes stipulated by the analytical method, by applicable regulations, or by other specific requirements must be spiked into the sample. Selection of the sample to be spiked and/or split depends on the information required and the variety of conditions within a typical matrix. In some situations, requirements of the site being sampled may dictate that the sampling team select a sample to be spiked and split based on a pre-visit evaluation or the on-site inspection. This does not preclude the laboratory's spiking a sample of its own selection as well. In other situations the laboratory may select the appropriate sample. The laboratory's selection should be guided by the objective of spiking, which is to determine the extent of matrix bias or interference on analyte recovery and sample-to-sample precision. For soil/sediment samples, spiking is performed at approximately 3 ppm and, therefore, compounds in excess of this concentration in the sample may cause interferences for the determination of the spiked analytes.

1.2.2.1.2 Blanks

Each batch shall be accompanied by a reagent blank. The reagent blank shall be carried through the entire analytical procedure.

1.2.2.1.3 Field Samples/Surrogate Compounds

Every blank, standard, and environmental sample (including matrix spike/matrix duplicate samples) shall be spiked with surrogate compounds prior to purging or extraction. Surrogates shall be spiked into samples according to the appropriate analytical methods. Surrogate spike recoveries shall fall within the control limits set by the laboratory (in accordance with procedures specified in the method or within ±20%) for samples falling within the quantification limits without dilution. Dilution of samples to bring the analyte concentration into the linear range of calibration may dilute the surrogates below the quantification limit; evaluation of analytical quality then will rely on the quality control embodied in the check, spiked and duplicate spiked samples.

1.2.2.1.4 Check Sample

Each analytical batch shall contain a check sample. The analytes employed shall be a representative subset of the analytes to be determined. The concentrations of these analytes shall approach the estimated quantification limit in the matrix of the check sample. In particular, check samples for metallic analytes shall be matched to field samples in phase and in general matrix composition.

1.2.2.2 Clean-Ups

Quality control procedures described here are intended for adsorbent chromatography and back extractions applied to organic extracts. All batches of adsorbents (Florisil, alumina, silica gel, etc.) prepared for use shall be checked for analyte recovery by running the elution pattern with standards as a column check. The elution pattern shall be optimized for maximum recovery of analytes and maximum rejection of contaminants.

1.2.2.2.1 Column Check Sample

The elution pattern shall be reconfirmed with a column check of standard compounds after activating or deactivating a batch of adsorbent. These compounds shall be representative of each elution fraction. Recovery as specified in the methods is considered an acceptable column check. A result lower than specified indicates that the procedure is not acceptable or has been misapplied.

1.2.2.2.2 Column Check Sample Blank

The check blank shall be run after activating or deactivating a batch of adsorbent.

1.2.2.3 Determinations

1.2.2.3.1 Instrument Adjustment: Tuning, Alignment, etc.

Requirements and procedures are instrument- and method-specific. Analytical instrumentation shall be tuned and aligned in accordance with requirements which are specific to the instrumentation procedures employed. Individual determinative procedures shall be consulted. Criteria for initial conditions and for continuing confirmation conditions for methods within this manual are found in the appropriate procedures.

1.2.2.3.2 Calibration

Analytical instrumentation shall be calibrated in accordance with requirements which are specific to the instrumentation and procedures employed. Introductory Methods 7000 and 8000 and appropriate analytical procedures shall be consulted for criteria for initial and continuing calibration.

1.2.2.3.3 Additional QC Requirements for Inorganic Analysis

Standard curves used in the determination of inorganic analytes shall be prepared as follows:

Standard curves derived from data consisting of one reagent blank and four concentrations shall be prepared for each analyte. The response for each prepared standard shall be based upon the average of three replicate readings of each standard. The standard curve shall be used with each subsequent analysis provided that the standard curve is verified by using at least one reagent blank and one standard at a level normally encountered or expected in such samples. The response for each standard shall be based upon the average of three replicate readings of the standard. If the results of the verification are not within ±10% of the original curve, a new standard shall be prepared and analyzed. If the results of the second verification are not within ±10% of the original standard curve, a reference standard should be employed to determine if the discrepancy is with the standard or with the instrument. New standards should also be prepared on a quarterly basis at a minimum. All data used in drawing or describing the curve shall be so indicated on the curve or its description. A record shall be made of the verification.

Standard deviations and relative standard deviations shall be calculated for the percent recovery of analytes from the spiked sample duplicates and from the check samples. These values shall be established for the twenty most recent determinations in each category.

1.2.2.3.4 Additional Quality Control Requirements for Organic Analysis

The following requirements shall be applied to the analysis of samples by gas chromatography, liquid chromatography and gas chromatography/mass spectrometry.

The calibration of each instrument shall be verified at frequencies specified in the methods. A new standard curve must be prepared as specified in the methods.

The tune of each GC/MS system used for the determination of organic analytes shall be checked with 4-bromofluorobenzene (BFB) for determinations of volatiles and with decafluorotriphenylphosphine (DFTPP) for determinations of semi-volatiles. The required ion abundance criteria shall be met before determination of any analytes. If the system does not meet the required specification for one or more of the required ions, the instrument must be retuned and rechecked before proceeding with sample analysis. The tune performance check criteria must be achieved daily or for each 12 hour operating period, whichever is more frequent.

Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. Background subtraction

actions resulting in spectral distortions for the sole purpose of meeting special requirements are contrary to the objectives of Quality Assurance and are unacceptable.

For determinations by HPLC or GC, the instrument calibration shall be verified as specified in the methods.

1.2.2.3.5 Identification

Identification of all analytes must be accomplished with an authentic standard of the analyte. When authentic standards are not available, identification is tentative.

For gas chromatographic determinations of specific analytes, the relative retention time of the unknown must be compared with that of an authentic standard. For compound confirmation, a sample and standard shall be re-analyzed on a column of different selectivity to obtain a second characteristic relative retention time. Peaks must elute within daily retention time windows to be declared a tentative or confirmed identification.

For gas chromatographic/mass spectrometric determinations of specific analytes, the spectrum of the analyte should conform to a literature representation of the spectrum or to a spectrum of the authentic standard obtained after satisfactory tuning of the mass spectrometer and within the same twelve-hour working shift as the analytical spectrum. The appropriate analytical methods should be consulted for specific criteria for matching the mass spectra, relative response factors, and relative retention times to those of authentic standards.

1.2.2.3.6 Quantification

The procedures for quantification of analytes are discussed in the appropriate general procedures (7000, 8000) and the specific analytical methods.

In some situations in the course of determining metal analytes, matrix-matched calibration standards may be required. These standards shall be composed of the pure reagent, approximation of the matrix, and reagent addition of major interferents in the samples. This will be stipulated in the procedures.

Estimation of the concentration of an organic compound not contained within the calibration standard may be accomplished by comparing mass spectral response of the compound with that of an internal standard. The procedure is specified in the methods.

1.3 DETECTION LIMIT AND QUANTIFICATION LIMIT

The detection limit and quantification limit of analytes shall be evaluated by determining the noise level of response for each sample in the batch. If analyte is present, the noise level adjacent in retention time to the analyte peak may be used. For wave-length dispersive instrumentation, multiple determinations of digestates with no detectable analyte may be used to establish the noise level. The method of standard additions should then be used to determine the calibration curve using one digestate or extracted sample in which the analyte was not detected. The slope of the calibration curve, m, should be calculated using the following relations:

m = slope of calibration line

S_B = standard deviation of the average noise level

$MDL = KS_B/m$

For K = 3; MDL = method detection limit.

For K = 5; MQL = method quantitation limit.

1.4 DATA REPORTING

The requirement of reporting analytical results on a wet-weight or a dry-weight basis is dictated by factors such as: sample matrix; program or regulatory requirement; and objectives of the analysis.

Analytical results shall be reported with the percent moisture or percent solid content of the sample.

1.5 QUALITY CONTROL DOCUMENTATION

The following sections list the QC documentation which comprises the complete analytical package. This package should be obtained from the data generator upon request. These forms, or adaptations of these forms, shall be used by the data generator/reportor for inorganics (I), or for organics (O) or both (I/O) types of determinations.

1.5.1 Analytical Results (I/O: Form I)

Analyte concentration.

Sample weight.

Percent water (for non-aqueous samples when specified).

Final volume of extract or diluted sample.

Holding times (I: Form X).

1.5.2 Calibration (I: Form II; O: Form V, VI, VII, IX)

Calibration curve or coefficients of the linear equation which describes the calibration curve.

Correlation coefficient of the linear calibration.

Concentration/response data (or relative response data) of the calibration check standards, along with dates on which they were analytically determined.

1.5.3 Column Check (O: Form X)

Results of column chromatography check, with the chromatogram.

1.5.4 Extraction/Digestion (I/O: Form I)

Date of the extraction for each sample.

1.5.5 Surrogates (O: Form II)

Amount of surrogate spiked, and percent recovery of each surrogate.

1.5.6 Matrix/Duplicate Spikes (I: Form V, VI; O: Form III)

Amount spiked, percent recovery, and relative percent difference for each compound in the spiked samples for the analytical batch.

1.5.7 Check Sample (I: Form VII; O: Form VIII)

Amount spiked, and percent recovery of each compound spiked.

1.5.8 Blank (I: Form III; O: Form IV)

Identity and amount of each constituent.

1.5.9 Chromatograms (for organic analysis)

All chromatograms for reported results, properly labeled with:

- Sample identification
- Method identification
- Identification of retention time of analyte on the chromatograms.

1.5.10 Quantitative Chromatogram Report (O: Forms VIII, IX, X)

Retention time of analyte.

Amount injected.

Area of appropriate calculation of detection response.

Amount of analyte found.

Date and time of injection.

1.5.11 Mass Spectrum

Spectra of standards generated from authentic standards (one for each report for each compound detected).

Spectra of analytes from actual analyses.

Spectrometer identifier.

1.5.12 Metal Interference Check Sample Results (I: Form IV)

1.5.13 Detection Limit (I: Form VII; O: Form I)

Analyte detection limits with methods of estimation.

1.5.14 Results of Standard Additions (I: Form VIII)

1.5.15 Results of Serial Dilutions (I: Form IX)

1.5.16 Instrument Detection Limits (I: Form XI)

1.5.17 ICP Interelement Correction Factors and ICP Linear Ranges (when applicable) (I: Form XII, Form XIII).

1.6 REFERENCES

1. Guidelines and Specifications for Preparing Quality Assurance Program Plans, September 20, 1980, Office of Monitoring Systems and Quality Assurance, ORD, U.S. EPA, QAMS-004/80, Washington, DC 20460.

2. Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans, December 29, 1980, Office of Monitoring Systems and Quality Assurance, ORD, U.S. EPA, QAMS-005/80, Washington, DC 20460.

Date _____

COVER PAGE
INORGANIC ANALYSES DATA PACKAGE

Lab Name _____ Case No. _____

No. _____ Q.C. Report No. _____

Sample Numbers

EPA No.	Lab ID No.	EPA No.	Lab ID No.

Comments: _____

Form I

Sample No.

Date _____

INORGANIC ANALYSIS DATA SHEET

LAB NAME _____ CASE NO. _____

Lab Receipt Date _____

LAB SAMPLE ID. NO. _____ QC REPORT NO. _____

Elements Identified and Measured

Matrix: Water _____ Soil _____ Sludge _____ Other _____

ug/L or mg/kg dry weight (Circle One)

1.	Aluminum	13.	Magnesium
2.	Antimony	14.	Manganese
3.	Arsenic	15.	Mercury
4.	Barium	16.	Nickel
5.	Beryllium	17.	Potassium
6.	Cadmium	18.	Selenium
7.	Calcium	19.	Silver
8.	Chromium	20.	Sodium
9.	Cobalt	21.	Thallium
10.	Copper	22.	Vanadium
11.	Iron	23.	Zinc
12.	Lead		Precent Solids (%)

Cyanide _____

Comments: _____

_____

_____

_____

Lab Manager _____

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Date September 1986

Form II

Q. C. Report No. _____

INITIAL AND CONTINUING CALIBRATION VERIFICATION

LAB NAME _____ CASE NO. _____

DATE _____ UNITS: ug/L

Compound	Initial Calib.[1]			Continuing Calibration[2]					
Metals:	True Value	Found	%R	True Value	Found	%R	Found	%R	Method[4]
1. Aluminum									
2. Antimony									
3. Arsenic									
4. Barium									
5. Beryllium									
6. Cadmium									
7. Calcium									
8. Chromium									
9. Cobalt									
10. Copper									
11. Iron									
12. Lead									
13. Magnesium									
14. Manganese									
15. Mercury									
16. Nickel									
17. Potassium									
18. Selenium									
19. Silver									
20. Sodium									
21. Thallium									
22. Vanadium									
23. Zinc									
Other: _____									
Cyanide									

[1] Initial Calibration Source

[2] Continuing Calibration Source _____

[4] Indicate Analytical Method Used: P - ICP; A - Flame AA; F - Furnace AA

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Form III

Q. C. Report No. _____

BLANKS

LAB NAME _____ CASE NO. _____

DATE _____ UNITS _____

Compound	Initial Calibration Blank Value	Continuing Calibration Blank Value 1	2	3	4	Preparation Blank Matrix: _____ 1	Matrix: _____ 2
Metals:							
1. Aluminum							
2. Antimony							
3. Arsenic							
4. Barium							
5. Beryllium							
6. Cadmium							
7. Calcium							
8. Chromium							
9. Cobalt							
10. Copper							
11. Iron							
12. Lead							
13. Magnesium							
14. Manganese							
15. Mercury							
16. Nickel							
17. Potassium							
18. Selenium							
19. Silver							
20. Sodium							
21. Thallium							
22. Vanadium							
23. Zinc							
Other: _____							
Cyanide							

[1] Reporting Units: aqueous, ug/L; solid mg/kg

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Form IV

Q. C. Report No. _____

ICP INTERFERENCE CHECK SAMPLE

LAB NAME _____ CASE NO. _____

Check Sample I.D. _____

DATE _____ Check Sample Source _____

Units: ug/L

Compound	Control Limits[1] Mean	Std. Dev.	True[2]	Initial Observed	%R	Final Observed	%R
Metals:							
1. Aluminum							
2. Antimony							
3. Arsenic							
4. Barium							
5. Beryllium							
6. Cadmium							
7. Calcium							
8. Chromium							
9. Cobalt							
10. Copper							
11. Iron							
12. Lead							
13. Magnesium							
14. Manganese							
15. Mercury							
16. Nickel							
17. Potassium							
18. Selenium							
19. Silver							
20. Sodium							
21. Thallium							
22. Vanadium							
23. Zinc							
Other: _____							

[1] Mean value based on n = _____.

[2] True value of EPA ICP Interference Check Sample or contractor standard.

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Form V

Q. C. Report No. _____

SPIKE SAMPLE RECOVERY

LAB NAME _____ CASE NO. _____

Sample No. _____

DATE _____ Lab Sample ID No. _____

Units _____

Matrix _____

Compound	Control Limit %R	Spiked Sample Result (SSR)	Sample Result (SR)	Spiked Added (SA)	%R[1]
Metals:					
1. Aluminum					
2. Antimony					
3. Arsenic					
4. Barium					
5. Beryllium					
6. Cadmium					
7. Calcium					
8. Chromium					
9. Cobalt					
10. Copper					
11. Iron					
12. Lead					
13. Magnesium					
14. Manganese					
15. Mercury					
16. Nickel					
17. Potassium					
18. Selenium					
19. Silver					
20. Sodium					
21. Thallium					
22. Vanadium					
23. Zinc					
Other:					
Cyanide					

[1] %R = [(SSR - SR)/SA] x 100

"N" - out of control

"NR" - Not required

Comments: _____

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Form VI

Q. C. Report No. _____

DUPLICATES

LAB NAME _____ CASE NO. _____

Sample No. _____

DATE _____ Lab Sample ID No. _____

Units _____

Matrix _____

Compound	Control Limit[1]	Sample(S)	Duplicate(D)	RPD[2]
Metals:				
1. Aluminum				
2. Antimony				
3. Arsenic				
4. Barium				
5. Beryllium				
6. Cadmium				
7. Calcium				
8. Chromium				
9. Cobalt				
10. Copper				
11. Iron				
12. Lead				
13. Magnesium				
14. Manganese				
15. Mercury				
16. Nickel				
17. Potassium				
18. Selenium				
19. Silver				
20. Sodium				
21. Thallium				
22. Vanadium				
23. Zinc				
Other:				
Cyanide				

* Out of Control

[1] To be added at a later date.

[2] RPD = [|S - D|/((S + D)/2)] x 100

NC - Non calculable RPD due to value(s) less than CRDL

Form VII

Q.C. Report No. _____

INSTRUMENT DETECTION LIMITS AND

LABORATORY CONTROL SAMPLE

LAB NAME _____ CASE NO. _____ DATE _____

LCS NO. _____

Compound	Required Detection Limits (CRDL)-ug/l	Instrument Detection Limits (IDL)-ug/l ICP/AA ID# _____	Instrument Detection Limits (IDL)-ug/l Furnace ID# _____	Lab Control Sample ug/L mg/kg (circle one) True	Found	%R
Metals:						
1. Aluminum						
2. Antimony						
3. Arsenic						
4. Barium						
5. Beryllium						
6. Cadmium						
7. Calcium						
8. Chromium						
9. Cobalt						
10. Copper						
11. Iron						
12. Lead						
13. Magnesium						
14. Manganese						
15. Mercury						
16. Nickel						
17. Potassium						
18. Selenium						
19. Silver						
20. Sodium						
21. Thallium						
22. Vanadium						
23. Zinc						
Other: _____						
Cyanide		NR	NR			

NR - Not required

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Form VIII

Q.C. Report No. _____

STANDARD ADDITION RESULTS

LAB NAME _____ CASE NO. _____

DATE _____ UNITS: ug/L

EPA Sample #	Element	Matrix	0 ADD ABS.	1 ADD CON.	1 ADD ABS.[2]	2 ADD CON.	2 ADD ABS.[2]	3 ADD CON.	3 ADD ABS.[2]	FINAL CON.[3]	r*

[2] CON is the concentration added, ABS. is the instrument readout in absorbance or concentration.

[3] Concentration as determined by MSA

*"r" is the correlation coefficient.

+ - correlation coefficient is outside of control window of 0.995.

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Form IX

Q. C. Report No. _____

ICP SERIAL DILUTIONS

LAB NAME _____ CASE NO. _____

Sample No. _____

DATE _____ Lab Sample ID No. _____

Units: ug/L

Matrix _____

Compound	Initial Sample Concentration(I)	Serial Dilution[1] Result(S)	% Difference[2]
Metals:			
1. Aluminum			
2. Antimony			
3. Arsenic			
4. Barium			
5. Beryllium			
6. Cadmium			
7. Calcium			
8. Chromium			
9. Cobalt			
10. Copper			
11. Iron			
12. Lead			
13. Magnesium			
14. Manganese			
15. Nickel			
16. Potassium			
17. Selenium			
18. Silver			
19. Sodium			
20. Thallium			
21. Vanadium			
22. Zinc			
Other: _____			

[1] Diluted sample concentration corrected for 1:4 dilution (see Exhibit D)

[2] Percent Difference = $\frac{|I - S|}{I} \times 100$

NR - Not Required, initial sample concentration less than 10 times IDL

NA - Not Applicable, analyte not determined by ICP

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Form X

QC Report No. _____

HOLDING TIMES

LAB NAME _____

DATE _____ CASE NO. _____

EPA Sample No.	Matrix	Date Received	Mercury Prep Date	Mercury Holding Time[1] (Days)	CN Prep Date	CN Holding Time[1] (Days)

[1]Holding time is defined as number of days between the date received and the sample preparation date.

Form XI

INSTRUMENT DETECTION LIMITS

LAB NAME _____ DATE _____

ICP/Flame AA (Circle One) Model Number _____ Furnace AA Number _____

Element	Wavelength (nm)	IDL (ug/L)	Element	Wavelength (nm)	IDL (ug/L)
1. Aluminum			13. Magnesium		
2. Antimony			14. Manganese		
3. Arsenic			15. Mercury		
4. Barium			16. Nickel		
5. Beryllium			17. Potassium		
6. Cadmium			18. Selenium		
7. Calcium			19. Silver		
8. Chromium			20. Sodium		
9. Cobalt			21. Thallium		
10. Copper			22. Vanadium		
11. Iron			23. Zinc		
12. Lead					

Footnotes:
- Indicate the instrument for which the IDL applies with a "P" (for ICP an "A" (for Flame AA), or an "F" (for Furnace AA) behind the IDL valu
- Indicate elements commonly run with background correction (AA) with a "B" behind the analytical wavelength.
- If more than one ICP/Flame or Furnace AA is used, submit separate Forms XI-XIII for each instrument.

COMMENTS: _____

Lab Manager _____

Revision 0
Date September 1986

Form XII

ICP Interelement Correction Factors

LABORATORY _____ ICP Model Number _____

DATE _____

Analyte	Analyte Wavelength (nm)	Interelement Correction Factors for Al	Ca	Fe	Mg				
1. Antimony									
2. Arsenic									
3. Barium									
4. Beryllium									
5. Cadmium									
6. Chromium									
7. Cobalt									
8. Copper									
9. Lead									
10. Manganese									
11. Mercury									
12. Nickel									
13. Potassium									
14. Selenium									
15. Silver									
16. Sodium									
17. Thallium									
18. Vanadium									
19. Zinc									

COMMENTS: _____

Lab Manager _____

Revision 0
Date September 1986

Form XII

ICP Interelement Correction Factors

LABORATORY _____ ICP Model Number _____

DATE _____

Analyte	Analyte Wavelength (nm)	Interelement Correction Factors for							
1. Antimony									
2. Arsenic									
3. Barium									
4. Beryllium									
5. Cadmium									
6. Chromium									
7. Cobalt									
8. Copper									
9. Lead									
10. Manganese									
11. Mercury									
12. Nickel									
13. Potassium									
14. Selenium									
15. Silver									
16. Sodium									
17. Thallium									
18. Vanadium									
19. Zinc									

COMMENTS: _____

Lab Manager _____

Form XIII

ICP Linear Ranges

LAB NAME _____ ICP Model Number _____

DATE _____

Analyte	Integration Time (Seconds)	Concentration (ug/L)	Analyte	Integration Time (Seconds)	Concentration (ug/L)
1. Aluminum			13. Magnesium		
2. Antimony			14. Manganese		
3. Arsenic			15. Mercury		
4. Barium			16. Nickel		
5. Beryllium			17. Potassium		
6. Cadmium			18. Selenium		
7. Calcium			19. Silver		
8. Chromium			20. Sodium		
9. Cobalt			21. Thallium		
10. Copper			22. Vanadium		
11. Iron			23. Zinc		
12. Lead					

Footnotes: • Indicate elements not analyzed by ICP with the notation "NA".

COMMENTS: _____

_____

_____

_____

Lab Manager _____

Revision 0
Date September 1986

Organics Analysis Data Sheet
(Page 1)

Sample Number

Laboratory Name: _____ Case No: _____

Lab Sample ID No: _____ QC Report No: _____

Sample Matrix: _____

Data Release Authorized By: _____ Date Sample Received: _____

Volatile Compounds

Date Extracted/Prepared: _____

Date Analyzed: _____

Conc/Dil Factor: _____ pH _____

Percent Moisture: (Not Decanted) _____

CAS Number		ug/l or ug/Kg (Circle One)
74-87-3	Chloromethane	
74-83-9	Bromomethane	
75-01-4	Vinyl Chloride	
75-00-3	Chloroethane	
75-09-2	Methylene Chloride	
67-64-1	Acetone	
75-15-0	Carbon Disulfide	
75-35-4	1, 1-Dichloroethene	
75-34-3	1, 1-Dichloroethane	
156-60-5	Trans-1, 2-Dichloroethene	
67-66-3	Chloroform	
107-06-2	1, 2-Dichloroethane	
78-93-3	2-Butanone	
71-55-6	1, 1, 1-Trichloroethane	
56-23-5	Carbon Tetrachloride	
108-05-4	Vinyl Acetate	
75-27-4	Bromodichloromethane	

CAS Number		ug/l or ug/Kg (Circle One)
78-87-5	1, 2-Dichloropropane	
10061-02-6	Trans-1, 3-Dichloropropene	
79-01-6	Trichloroethene	
124-48-1	Dibromochloromethane	
79-00-5	1, 1, 2-Trichloroethane	
71-43-2	Benzene	
10061-01-5	cis-1, 3-Dichloropropene	
110-75-8	2-Chloroethylvinylether	
75-25-2	Bromoform	
108-10-1	4-Methyl-2-Pentanone	
591-78-6	2-Hexanone	
127-18-4	Tetrachloroethene	
79-34-5	1, 1, 2, 2-Tetrachloroethane	
108-88-3	Toluene	
108-90-7	Chlorobenzene	
100-41-4	Ethylbenzene	
100-42-5	Styrene	
	Total Xylenes	

Data Reporting Qualifiers

For reporting results to EPA, the following results qualifiers are used. Additional flags or footnotes explaining results are encouraged. However, the definition of each flag must be explicit.

Value If the result is a value greater than or equal to the detection limit, report the value.

U Indicates compound was analyzed for but not detected. Report the minimum detection limit for the sample with the U (e.g., 10U) based on necessary concentration/dilution action. (This is not necessarily the instrument detection limit.) The footnote should read "U - Compound was analyzed for but not detected. The number is the minimum attainable detection limit for the sample."

J Indicates an estimated value. This flag is used either when estimating a concentration for tentatively identified compounds where a 1:1 response is assumed or when the mass spectral data indicated the presence of a compound that meets the identification criteria but the result is less than the specified detection limit but greater than zero (e.g., 10J). If limit of detection is 10 µg/l and a concentration of 3 µg/l is calculated, report as 3J.

C This flag applies to pesticide parameters where the identification has been confirmed by GC/MS. Single component pesticides ≥ 10 ng/ml in the final extract should be confirmed by GC/MS.

B This flag is used when the analyte is found in the blank as well as a sample. It indicates possible/probable blank contamination and warns the data user to take appropriate action.

Other Other specific flags and footnotes may be required to properly define the results. If used, they must be fully described and such description attached to the data summary report.

Form I

Revision 0
Date September 1986

Laboratory Name _____

Case No. _____

Sample Number

Organics Analysis Data Sheet
(Page 2)

Semivolatile Compounds

GPC Cleanup ☐Yes ☐No

Date Extracted/Prepared: _____

Separatory Funnel Extraction ☐Yes

Date Analyzed: _____

Continuous Liquid - Liquid Extraction ☐Yes

Conc/Dil Factor: _____

Percent Moisture (Decanted) _____

CAS Number		ug/l or ug/Kg (Circle One)
108-95-2	Phenol	
111-44-4	bis(-2-Chloroethyl)Ether	
95-57-8	2-Chlorophenol	
541-73-1	1, 3-Dichlorobenzene	
106-46-7	1, 4-Dichlorobenzene	
100-51-6	Benzyl Alcohol	
95-50-1	1, 2-Dichlorobenzene	
95-48-7	2-Methylphenol	
39638-32-9	bis(2-chloroisopropyl)Ether	
106-44-5	4-Methylphenol	
621-64-7	N-Nitroso-Di-n-Propylamine	
67-72-1	Hexachloroethane	
98-95-3	Nitrobenzene	
78-59-1	Isophorone	
88-75-5	2-Nitrophenol	
105-67-9	2, 4-Dimethylphenol	
65-85-0	Benzoic Acid	
111-91-1	bis(-2-Chloroethoxy)Methane	
120-83-2	2, 4-Dichlorophenol	
120-82-1	1, 2, 4-Trichlorobenzene	
91-20-3	Naphthalene	
106-47-8	4-Chloroaniline	
87-68-3	Hexachlorobutadiene	
59-50-7	4-Chloro-3-Methylphenol	
91-57-6	2-Methylnaphthalene	
77-47-4	Hexachlorocyclopentadiene	
88-06-2	2, 4, 6-Trichlorophenol	
95-95-4	2, 4, 5-Trichlorophenol	
91-58-7	2-Chloronaphthalene	
88-74-4	2-Nitroaniline	
131-11-3	Dimethyl Phthalate	
208-96-8	Acenaphthylene	
99-09-2	3-Nitroaniline	

CAS Number		ug/l or ug/Kg (Circle One)
83-32-9	Acenaphthene	
51-28-5	2, 4-Dinitrophenol	
100-02-7	4-Nitrophenol	
132-64-9	Dibenzofuran	
121-14-2	2, 4-Dinitrotoluene	
606-20-2	2, 6-Dinitrotoluene	
84-66-2	Diethylphthalate	
7005-72-3	4-Chlorophenyl-phenylether	
86-73-7	Fluorene	
100-01-6	4-Nitroaniline	
534-52-1	4, 6-Dinitro-2-Methylphenol	
86-30-6	N-Nitrosodiphenylamine (1)	
101-55-3	4-Bromophenyl-phenylether	
118-74-1	Hexachlorobenzene	
87-86-5	Pentachlorophenol	
85-01-8	Phenanthrene	
120-12-7	Anthracene	
84-74-2	Di-n-Butylphthalate	
206-44-0	Fluoranthene	
129-00-0	Pyrene	
85-68-7	Butylbenzylphthalate	
91-94-1	3, 3'-Dichlorobenzidine	
56-55-3	Benzo(a)Anthracene	
117-81-7	bis(2-Ethylhexyl)Phthalate	
218-01-9	Chrysene	
117-84-0	Di-n-Octyl Phthalate	
205-99-2	Benzo(b)Fluoranthene	
207-08-9	Benzo(k)Fluoranthene	
50-32-8	Benzo(a)Pyrene	
193-39-5	Indeno(1, 2, 3-cd)Pyrene	
53-70-3	Dibenz(a, h)Anthracene	
191-24-2	Benzo(g, h, i)Perylene	

(1)-Cannot be separated from diphenylamine

Laboratory Name: _____

Case No: _____

Sample Number

Organics Analysis Data Sheet
(Page 3)

Pesticide/PCBs

GPC Cleanup ☐Yes ☐No

Date Extracted/Prepared: _____

Separatory Funnel Extraction ☐Yes

Date Analyzed: _____

Continuous Liquid - Liquid Extraction ☐Yes

Conc/Dil Factor: _____

Percent Moisture (decanted) _____

CAS Number		ug/l or ug/Kg (Circle One)
319-84-6	Alpha-BHC	
319-85-7	Beta-BHC	
319-86-8	Delta-BHC	
58-89-9	Gamma-BHC (Lindane)	
76-44-8	Heptachlor	
309-00-2	Aldrin	
1024-57-3	Heptachlor Epoxide	
959-98-8	Endosulfan I	
60-57-1	Dieldrin	
72-55-9	4, 4'-DDE	
72-20-8	Endrin	
33213-65-9	Endosulfan II	
72-54-8	4, 4'-DDD	
1031-07-8	Endosulfan Sulfate	
50-29-3	4, 4'-DDT	
72-43-5	Methoxychlor	
53494-70-5	Endrin Ketone	
57-74-9	Chlordane	
8001-35-2	Toxaphene	
12674-11-2	Aroclor-1016	
11104-28-2	Aroclor-1221	
11141-16-5	Aroclor-1232	
53469-21-9	Aroclor-1242	
12672-29-6	Aroclor-1248	
11097-69-1	Aroclor-1254	
11096-82-5	Aroclor-1260	

V_i = Volume of extract injected (ul)

V_s = Volume of water extracted (ml)

W_s = Weight of sample extracted (g)

V_t = Volume of total extract (ul)

V_s _____ or W_s _____ V_t _____ V_i _____

Laboratory Name: _____

Case No: _____

Sample Number

Organics Analysis Data Sheet

	CAS Number	Compound Name	Fraction	RT or Scan Number	Estimated Concentration (ug/l or ug/kg)
1.					
2.					
3.					
4.					
5.					
6.					
7.					
8.					
9.					
10.					
11.					
12.					
13.					
14.					
15.					
16.					
17.					
18.					
19.					
20.					
21.					
22.					
23.					
24.					
25.					
26.					
27.					
28.					
29.					
30.					

Form 1, Part B

Revision 0
Date September 1986

WATER SURROGATE PERCENT RECOVERY SUMMARY

Case No. _____ **Laboratory Name** _____

	VOLATILE			SEMI-VOLATILE								PESTICIDE
SAMPLE NO.	TOLUENE-D8 (88-110)	BFB (86-115)	1,2 DICHLOROETHANE-D4 (76-114)	NITROBENZENE-D5 (35-114)	2-FLUOROBIPHENYL (43-116)	TERPHENYL-D14 (33-141)			PHENOL-D5 (10-94)	2-FLUOROPHENOL (21-100)	2,4,6 TRIBROMOPHENOL (10-123)	DIBUTYLCHLORENDATE (24-154)

VALUES ARE OUTSIDE OF REQUIRED QC LIMITS

Volatiles: _____ out of _____ ; outside of QC limits
Semi-Volatiles: _____ out of _____ ; outside of QC limits
Pesticides: _____ out of _____ ; outside of QC limits

Comments: _____

FORM II

ONE - 37

Revision 0
Date September 1986

SOIL SURROGATE PERCENT RECOVERY SUMMARY

Case No. _____ Laboratory Name _____

	VOLATILE			SEMI-VOLATILE								PESTICIDE
SAMPLE NO.	TOLUENE-D8 (81-117)	BFB (74-121)	1,2 DICHLOROETHANE-D4 (70-121)	NITROBENZENE-D5 (23-120)	2-FLUOROBIPHENYL (30-115)	TERPHENYL-D14 (18-137)			PHENOL-D5 (24-113)	2-FLUOROPHENOL (25-121)	2,4,6 TRIBROMOPHENOL (19-122)	DIBUTYLCHLORENDATE (20-150)

VALUES ARE OUTSIDE OF REQUIRED QC LIMITS

Volatiles: _____ out of _____ ; outside of QC limits
Semi-Volatiles: _____ out of _____ ; outside of QC limits
Pesticides: _____ out of _____ ; outside of QC limits

Comments: _____

FORM II

Revision 0
Date September 1986

WATER MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Case No. _____ **Laboratory Name** _____

FRACTION	COMPOUND	CONC. SPIKE ADDED (ug/L)	SAMPLE RESULT	CONC. MS	% REC	CONC. MSD	% REC	RPD	QC LIMITS RPD	QC LIMITS RECOVERY
VOA	1,1-Dichloroethene								14	61-145
	Trichloroethene								14	71-120
SAMPLE NO.	Chlorobenzene								13	75-130
	Toluene								13	76-125
_____	Benzene								11	76-127
B/N	1,2,4-Trichlorobenzene								28	39-98
	Acenaphthene								31	46-118
	2,4 Dinitrotoluene								38	24-96
SAMPLE NO.	Di-n-Butylphthalate								40	11-117
	Pyrene								31	26-127
	N-Nitroso-Di-n-Propylamine								38	41-116
_____	1,4-Dichlorobenzene								28	36-97
ACID	Pentachlorophenol								50	9-103
	Phenol								42	12-89
	2-Chlorophenol								40	27-123
SAMPLE NO.	4-Chloro-3-Methylphenol								42	23-97
	4-Nitrophenol								50	10-80
_____										
PEST	Lindane								15	56-123
	Heptachlor								20	40-131
	Aldrin								22	40-120
SAMPLE NO.	Dieldrin								18	52-126
	Endrin								21	56-121
_____	4,4'-DDT								27	38-127

ADVISORY LIMITS

RPD: VOAs _____ out of _____ ; outside QC limits
B/N _____ out of _____ ; outside QC limits
ACID _____ out of _____ ; outside QC limits
PEST _____ out of _____ ; outside QC limits

RECOVERY: VOAs _____ out of _____ ; outside QC limits
B/N _____ out of _____ ; outside QC limits
ACID _____ out of _____ ; outside QC limits
PEST _____ out of _____ ; outside QC limits

Comments: _____

SOIL MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Case No. _____ **Laboratory Name** _____

FRACTION	COMPOUND	CONC. SPIKE ADDED (ug/Kg)	SAMPLE RESULT	CONC. MS	% REC	CONC. MSD	% REC	RPD	QC LIMITS RPD	QC LIMITS RECOVERY
VOA	1,1-Dicholorethene								22	59-172
	Trichloroethene								24	62-137
SAMPLE NO.	Chlorobenzene								21	60-133
	Toluene								21	59-139
_____	Benzene								21	66-142
B/N	1,2,4-Trichlorobenzene								23	38-107
	Acenaphthene								19	31-137
	2,4 Dinitrotoluene								47	28-89
SAMPLE NO.	Di-n-Butylphthalate								47	29-135
	Pyrene								36	35-142
	N-Nitrosodi-n-Propylamine								38	41-126
_____	1,4-Dichlorobenzene								27	28-104
ACID	Pentachlorophenol								47	17-109
	Phenol								35	26-90
	2-Chlorophenol								50	25-102
SAMPLE NO.	4-Chloro-3-Methylphenol								33	26-103
_____	4-Nitrophenol								50	11-114
PEST	Lindane								50	46-127
	Heptachlor								31	35-130
	Aldrin								43	34-132
SAMPLE NO.	Dieldrin								38	31-134
	Endrin								45	42-139
_____	4,4'-DDT								50	23-134

ADVISORY LIMITS

RPD: VOAs ____ out of ____; outside QC limits
B/N ____ out of ____; outside QC limits
ACID ____ out of ____; outside QC limits
PEST ____ out of ____; outside QC limits

RECOVERY: VOAs ____ out of ____; outside QC limits
B/N ____ out of ____; outside QC limits
ACID ____ out of ____; outside QC limits
PEST ____ out of ____; outside QC limits

Comments: _____

FORM III

Revision 0
Date September 1986

METHOD BLANK SUMMARY

Case No. _____ **Laboratory Name** _____

FILE ID	DATE OF ANALYSIS	FRACTION	MATRIX	CONC. LEVEL	INST. ID	CAS NUMBER	COMPOUND (NSL.TIC OR UNKNOWN)	CONC.	UNITS	CRDL

Comments:

GC/MS TUNING AND MASS CALIBRATION
Bromofluorobenzene (BFB)

Case No. _____ Laboratory Name _____

Instrument ID _____ Date _____ Time _____

Data Release Authorized By: _____

m/e	ION ABUNDANCE CRITERIA	%RELATIVE ABUNDANCE
50	15.0 - 40.0% of the base peak	
75	30.0 - 60.0% of the base peak	
95	Base peak, 100% relative abundance	
96	5.0 - 9.0% of the base peak	
173	Less than 1.0% of the base peak	
174	Greater than 50.0% of the base peak	
175	5.0 - 9.0% of mass 174	( )[1]
176	Greater than 95.0%, but less than 101.0% of mass 174	( )[1]
177	5.0 - 9.0% of mass 176	( )[2]

THIS PERFORMANCE TUNE APPLIES TO THE FOLLOWING SAMPLES, BLANKS AND STANDARDS.

[1]Value in parenthesis is % mass 174.
[2]Value in parenthesis is % mass 176.

SAMPLE ID	LAB ID	DATE OF ANALYSIS	TIME OF ANALYSIS

FORM V

Revision 0
Date September 1986

GC/MS TUNING AND MASS CALIBRATION
Decafluorotriphenylphosphine (DFTPP)

Case No. _____ Laboratory Name _____

Instrument ID _____ Date _____ Time _____

Data Release Authorized By: _____

m/e	ION ABUNDANCE CRITERIA	%RELATIVE ABUNDANCE
51	30.0 - 60.0% of mass 198	
68	less than 2.0% of mass 69	( )[1]
69	mass 69 relative abundance	
70	less than 2.0% of mass 69	( )[1]
127	40.0 - 60.0% of mass 198	
197	less than 1.0% of mass 198	
198	base peak, 100% relative abundance	
199	5.0 - 9.0% of mass 198	
275	10.0 - 30.0% of mass 198	
365	greater than 1.00% of mass 198	
441	present, but less than mass 443	
442	greater than 40.0% of mass 198	
443	17.0 - 23.0% of mass 442	( )[2]

THIS PERFORMANCE TUNE APPLIES TO THE FOLLOWING SAMPLES, BLANKS AND STANDARDS.

[1]Value in parenthesis is % mass 69.
[2]Value in parenthesis is % mass 442.

SAMPLE ID	LAB ID	DATE OF ANALYSIS	TIME OF ANALYSIS

FORM V

Revision 0
Date September 1986

Initial Calibration Data
Volatile HSL Compounds

Case No: _____ Instrument I D: _____

Laboratory Name _____ Calibration Date: _____

Minimum $\overline{RF}$ for SPCC is 0.300 (0.25 for Bromoform) Maximum % RSD for CCC is 30%

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{100}	RF_{150}	RF_{200}	$\overline{RF}$	% RSD	CCC* SPCC**
Chloromethane								**
Bromomethane								
Vinyl Chloride								*
Chloroethane								
Methylene Chloride								
Acetone								
Carbon Disulfide								
1, 1-Dichloroethene								*
1, 1-Dichloroethane								**
Trans-1, 2-Dichloroethene								
Chloroform								*
1, 2-Dichloroethane								
2-Butanone								
1, 1, 1-Trichloroethane								
Carbon Tetrachloride								
Vinyl Acetate								
Bromodichloromethane								
1, 2-Dichloropropane								*
Trans-1, 3-Dichloropropene								
Trichloroethene								
Dibromochloromethane								
1, 1, 2-Trichloroethane								
Benzene								
cis-1, 3-Dichloropropene								
2-Chloroethylvinylether								
Bromoform								**
4-Methyl-2-Pentanone								
2-Hexanone								
Tetrachloroethene								
1, 1, 2, 2-Tetrachloroethane								**
Toluene								*
Chlorobenzene								**
Ethylbenzene								*
Styrene								
Total Xylenes								

RF -Response Factor (subscript is the amount of ug/L)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation

CCC -Calibration Check Compounds (*)
SPCC -System Performance Check Compounds (**)

Form VI

Initial Calibration Data
Volatile HSL Compounds

Case No: ____________ Instrument I D: ____________

Laboratory Name ____________ Calibration Date: ____________

Minimum $\overline{RF}$ for SPCC is **0.300** (0.25 for Bromoform)   Maximum % RSD for CCC is 30%

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{100}	RF_{150}	RF_{200}	$\overline{RF}$	% RSD	CCC• SPCC••

RF -Response Factor (subscript is the amount of ug/L)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation

CCC -Calibration Check Compounds (•)
SPCC -System Performance Check Compounds (••)

Form VI

Initial Calibration Data
Semivolatile HSL Compounds
(Page 1)

Case No: _____ Instrument ID: _____

Laboratory Name _____ Calibration Date: _____

Minimum $\overline{RF}$ for SPCC is 0.050 Maximum % RSD for CCC is 30%

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{80}	RF_{120}	RF_{160}	$\overline{RF}$	%RSD	CCC* SPCC**
Phenol								*
bis(-2-Chloroethyl)Ether								
2-Chlorophenol								
1, 3-Dichlorobenzene								
1, 4-Dichlorobenzene								*
Benzyl Alcohol								
1, 2-Dichlorobenzene								
2-Methylphenol								
bis(2-chloroisopropyl)Ether								
4-Methylphenol								
N-Nitroso-Di-n-Propylamine								**
Hexachloroethane								
Nitrobenzene								
Isophorone								
2-Nitrophenol								*
2, 4-Dimethylphenol								
Benzoic Acid	†							
bis(-2-Chloroethoxy)Methane								
2, 4-Dichlorophenol								*
1, 2, 4-Trichlorobenzene								
Naphthalene								
4-Chloroaniline								
Hexachlorobutadiene								*
4-Chloro-3-Methylphenol								*
2-Methylnaphthalene								
Hexachlorocyclopentadiene								**
2, 4, 6-Trichlorophenol								*
2, 4, 5-Trichlorophenol	†							
2-Chloronaphthalene								
2-Nitroaniline	†							
Dimethyl Phthalate								
Acenaphthylene								
3-Nitroaniline	†							
Acenaphthene								*
2, 4-Dinitrophenol	†							**
4-Nitrophenol	†							**
Dibenzofuran								

Response Factor (subscript is the amount of nanograms)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation
CCC -Calibration Check Compounds (*)
SPCC -System Performance Check Compounds (**)
† -Not detectable at 20 ng

Form VI

Revision 0
Date September 1986

Initial Calibration Data
Semivolatile HSL Compounds
(Page 2)

Case No: _____ Instrument ID: _____

Laboratory Name _____ Calibration Date: _____

Minimum $\overline{RF}$ for SPCC is 0.050 Maximum % RSD for CCC is 30%

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{80}	RF_{120}	RF_{160}	$\overline{RF}$	% RSD	CCC* SPCC**
2, 4-Dinitrotoluene								
2, 6-Dinitrotoluene								
Diethylphthalate								
4-Chlorophenyl-phenylether								
Fluorene								
4-Nitroaniline	†							
4, 6-Dinitro-2-Methylpheno!	†							
N-Nitrosodiphenylamine (1)								*
4-Bromophenyl-phenylether								
Hexachlorobenzene								
Pentachloropheno!	†							*
Phenanthrene								
Anthracene								
Di-N-Butylphthalate								
Fluoranthene								*
Pyrene								
Butylbenzylphthalate								
3, 3'-Dichlorobenzidine								
Benzo(a)Anthracene								
bis(2-Ethylhexyl)Phthalate								
Chrysene								
Di-n-Octyl Phthalate								*
Benzo(b)Fluoranthene								
Benzo(k)Fluoranthene								
Benzo(a)Pyrene								*
Indeno(1, 2, 3-cd)Pyrene								
Dibenz(a, h)Anthracene								
Benzo(g, h, i)Perylene								

Response Factor (subscript is the amount of nanograms)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation
CCC -Calibration Check Compounds (*)
SPCC -System Performance Check Compounds (**)
† - Not detectable at 20 ng
(1) - Cannot be separated from diphenylamine

Form VI

Initial Calibration Data
Semivolatile HSL Compounds
(Page 1)

Case No ______________ Instrument ID ______________________________

Laboratory Name ______________________________ Calibration Date ______________________________

Minimum $\overline{RF}$ for SPCC is 0.050 Maximum % RSD for CCC is 30%

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{80}	RF_{120}	RF_{160}	$\overline{RF}$	% RSD	CCC• SPCC••

Response Factor (subscript is the amount of nanograms)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation
CCC -Calibration Check Compounds (•)
SPCC -System Performance Check Compounds (••)
† -Not detectable at 20 ng

Form VI

Revision 0
Date September 1986

Continuing Calibration Check
Volatile HSL Compounds

Case No: _____ Calibration Date: _____

Laboratory Name _____ Time: _____

Contract No: _____ **Laboratory ID:** _____

Instrument ID: _____ Initial Calibration Date: _____

Minimum RF for SPCC is 0.300 (0.25 for Bromoform) Maximum %D for CCC is 25%

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC
Chloromethane					••
Bromomethane					
Vinyl Chloride				•	
Chloroethane					
Methylene Chloride					
Acetone					
Carbon Disulfide					
1, 1-Dichloroethene				•	
1, 1-Dichloroethane					••
Trans-1, 2-Dichloroethene					
Chloroform				•	
1, 2-Dichloroethane					
2-Butanone					
1, 1, 1-Trichloroethane					
Carbon Tetrachloride					
Vinyl Acetate					
Bromodichloromethane					
1, 2-Dichloropropane				•	
Trans-1, 3-Dichloropropene					
Trichloroethene					
Dibromochloromethane					
1, 1, 2-Trichloroethane					
Benzene					
cis-1, 3-Dichloropropene					
2-Chloroethylvinylether					
Bromoform					••
4-Methyl-2-Pentanone					
2-Hexanone					
Tetrachloroethene					
1, 1, 2, 2-Tetrachloroethane					••
Toluene				•	
Chlorobenzene					••
Ethylbenzene				•	
Styrene					
Total Xylenes					

RF_{50} -Response Factor from daily standard file at 50 ug/l
RF -Average Response Factor from initial calibration Form VI

%D -Percent Difference
CCC -Calibration Check Compounds (•)
SPCC -System Performance Check Compounds (••)

Form VII

Revision 0
Date September 1986

Continuing Calibration Check
Volatile HSL Compounds

Case No. ____________ Calibration Date ____________

Laboratory Name ____________ Time ____________

Contract No: ____________ Laboratory ID: ____________

Instrument ID: ____________ Initial Calibration Date ____________

Minimum RF for SPCC is **0.300** (0.25 for Bromoform) Maximum %D for CCC is **25%**

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC

RF_{50} - Response Factor from daily standard file at 50 ug/l
$\overline{RF}$ - Average Response Factor from initial calibration Form VI
%D - Percent Difference
CCC - Calibration Check Compounds (*)
SPCC - System Performance Check Compounds (**)

Form VII

Revision 0
Date September 1986

Continuing Calibration Check
Semivolatile HSL Compounds
(Page 1)

Case No: _____ Calibration Date: _____

Laboratory Name_____ Time: _____

Laboratory ID: _____

Instrument ID: _____ Initial Calibration Date: _____

Minimum RF for SPCC is 0.050 Maximum %D for CCC is 25%

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC
Phenol				*	
bis(-2-Chloroethyl)Ether					
2-Chlorophenol					
1, 3-Dichlorobenzene					
1, 4-Dichlorobenzene				*	
Benzyl Alcohol					
1, 2-Dichlorobenzene					
2-Methylphenol					
bis(2-chloroisopropyl)Ether					
4-Methylphenol					
N-Nitroso-Di-n-Propylamine					* *
Hexachloroethane					
Nitrobenzene					
Isophorone					
2-Nitrophenol				*	
2, 4-Dimethylphenol					
Benzoic Acid †					
bis(-2-Chloroethoxy)Methane					
2, 4-Dichlorophenol				*	
1, 2, 4-Trichlorobenzene					
Naphthalene					
4-Chloroaniline					
Hexachlorobutadiene				*	
4-Chloro-3-Methylphenol				*	
2-Methylnaphthalene					
Hexachlorocyclopentadiene					* *
2, 4, 6-Trichlorophenol				*	
2, 4, 5-Trichlorophenol †					
2-Chloronaphthalene					
2-Nitroaniline †					
Dimethyl Phthalate					
Acenaphthylene					
3-Nitroaniline †					
Acenaphthene				*	
2, 4-Dinitrophenol †					* *
4-Nitrophenol †					* *
Dibenzofuran					

RF_{50} -Response Factor from daily standard file at concentration indicated (50 total nanograms)

$\overline{RF}$ -Average Response Factor from initial calibration Form VI

†-Due to low response, analyze at 80 total nanograms

%D -Percent Difference

CCC -Calibration Check Compounds (•)

SPCC -System Performance Check Compounds (••)

Continuing Calibration Check
Semivolatile HSL Compounds
(Page 2)

Case No: _____ Calibration Date: _____

Laboratory Name _____ *Time*: _____

Laboratory ID: _____

Instrument ID: _____ Initial Calibration Date: _____

Minimum RF for SPCC is 0.050 Maximum %D for CCC is 25%

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC
2, 4-Dinitrotoluene					
2, 6-Dinitrotoluene					
Diethylphthalate					
4-Chlorophenyl-phenylether					
Fluorene					
4-Nitroaniline †					
4, 6-Dinitro-2-Methylphenol †					
N-Nitrosodiphenylamine (1)				•	
4-Bromophenyl-phenylether					
Hexachlorobenzene					
Pentachlorophenol †				•	
Phenanthrene					
Anthracene					
Di-N-Butylphthalate					
Fluoranthene				•	
Pyrene					
Butylbenzylphthalate					
3, 3'-Dichlorobenzidine					
Benzo(a)Anthracene					
bis(2-Ethylhexyl)Phthalate					
Chrysene					
Di-n-Octyl Phthalate				•	
Benzo(b)Fluoranthene					
Benzo(k)Fluoranthene					
Benzo(a)Pyrene				•	
Indeno(1, 2, 3-cd)Pyrene					
Dibenz(a, h)Anthracene					
Benzo(g, h, i)Perylene					

RF_{50} -Response Factor from daily standard file at concentration indicated (50 total nanograms)

$\overline{RF}$ -Average Response Factor from initial calibration Form VI

%D Percent Difference

† -Due to low response, analyze at 80 total nanograms

CCC -Calibration Check Compounds (•)

SPCC -System Performance Check Compounds (••)

(1) -Cannot be separated from diphenylamine

Form VII

Continuing Calibration Check
Semivolatile HSL Compounds
(Page 1)

Case No: ______________ Calibration Date: ______________

Laboratory Name ______________ Time: ______________

Laboratory ID: ______________

Instrument ID: ______________ Initial Calibration Date: ______________

Minimum RF for SPCC is 0.050 Maximum %D for CCC is 25%

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC

RF_{50} -Response Factor from daily standard file at concentration indicated (50 total nanograms)

$\overline{RF}$ -Average Response Factor from initial calibration Form VI

† -Due to low response, analyze at 80 total nanograms

%D -Percent Difference

CCC -Calibration Check Compounds (•)

SPCC System Performance Check Compounds (••)

Form VII

Pesticide Evaluation Standards Summary
(Page 1)

Case No: _____ **Laboratory Name**: _____

GC Column: _____

Date of Analysis _____ Instrument ID: _____

Evaluation Check for Linearity

Laboratory ID				
Pesticide	Calibration Factor Eval. Mix A	Calibration Factor Eval. Mix B	Calibration Factor Eval. Mix C	% RSD (≤10%)
Aldrin				
Endrin				
4,4 - DDT(1)				
Dibutyl Chlorendate				

Evaluation Check for 4,4'- DDT/Endrin Breakdown
(percent breakdown expressed as total degradation)

	Laboratory I.D.	Time of Analysis	Endrin	4,4'- DDT	Combined(2)
Eval Mix B 72 Hour					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					

(1) See Exhibit E, Section 7.5.4
(2) See Exhibit E, Section 7.3.1.2.2.1

Form VIII

RCRA 4/86

Pesticide Evaluation Standards Summary

(Page 2)

Evaluation of Retention Time Shift for Dibutyl Chlorendate

Report all standards, blanks and samples

Sample No	Lab I.D	Time of Analysis	Percent Diff.	SMO Sample No.	Lab I.D.	Time of Analysis	Percent Diff.

Form VIII (Continued)

RCRA
4/86

PESTICIDE/PCB STANDARDS SUMMARY

Case No. _____ Laboratory Name _____

GC Column _____ GC Instrument ID _____

	DATE OF ANALYSIS _____ TIME OF ANALYSIS _____ LABORATORY ID _____				DATE OF ANALYSIS _____ TIME OF ANALYSIS _____ LABORATORY ID _____			
COMPOUND	RT	RETENTION TIME WINDOW	CALIBRATION FACTOR	CONF. OR QUANT.	RT	CALIBRATION FACTOR	CONF. OR QUANT.	PERCENT DIFF. **
alpha-BHC								
beta-BHC								
delta-BHC								
gamma-BHC								
Heptachlor								
Aldrin								
Heptachlor Epoxide								
Endosulfan I								
Dieldrin								
4,4'-DDE								
Endrin								
Endosulfan II								
4,4'-DDD								
Endrin Aldehyde								
Endosulfan Sulfate								
4,4'-DDT								
Methoxychlor								
Endrin Ketone								
Tech. Chlordane								
alpha-Chlordane								
gamma-Chlordane								
Toxaphene								
Aroclor - 1016								
Aroclor - 1221								
Aroclor - 1232								
Aroclor - 1242								
Aroclor - 1248								
Aroclor - 1254								
Aroclor - 1260								

** CONF. = CONFIRMATION (<20% DIFFERENCE)
QUANT. = QUANTITATION (<15% DIFFERENCE)

FORM IX

Revision 0
Date September 1986

Pesticide/PCB Identification

Case No. ____________________ **Laboratory Name** ____________________

SAMPLE ID	PRIMARY COLUMN	PESTICIDE/ PCB	RT OF TENTATIVE ID	RT WINDOW OF APPROPRIATE STANDARD	CONFIRMATION COLUMN	RT ON CONFIRMATORY COLUMN	RT WINDOW OF APPROPRIATE STANDARD	GC/MS CONFIRMED (Y or N)

FORM X

PART III SAMPLING

CHAPTER NINE

SAMPLING PLAN

9.1 DESIGN AND DEVELOPMENT

The initial -- and perhaps most critical -- element in a program designed to evaluate the physical and chemical properties of a solid waste is the plan for sampling the waste. It is understandable that analytical studies, with their sophisticated instrumentation and high cost, are often perceived as the dominant element in a waste characterization program. Yet, despite that sophistication and high cost, analytical data generated by a scientifically defective sampling plan have limited utility, particularly in the case of regulatory proceedings.

This section of the manual addresses the development and implementation of a scientifically credible sampling plan for a solid waste and the documentation of the chain of custody for such a plan. The information presented in this section is relevant to the sampling of any solid waste, which has been defined by the EPA in its regulations for the identification and listing of hazardous wastes to include solid, semisolid, liquid, and contained gaseous materials. However, the physical and chemical diversity of those materials, as well as the dissimilarity of storage facilities (lagoons, open piles, tanks, drums, etc.) and sampling equipment associated with them, preclude a detailed consideration of any specific sampling plan. Consequently, because the burden of responsibility for developing a technically sound sampling plan rests with the waste producer, it is advisable that he/she seek competent advice before designing a plan. This is particularly true in the early developmental stages of a sampling plan, at which time at least a basic understanding of applied statistics is required. Applied statistics is the science of employing techniques that allow the uncertainty of inductive inferences (general conclusions based on partial knowledge) to be evaluated.

9.1.1 Development of Appropriate Sampling Plans

An appropriate sampling plan for a solid waste must be responsive to both regulatory and scientific objectives. Once those objectives have been clearly identified, a suitable sampling strategy, predicated upon fundamental statistical concepts, can be developed. The statistical terminology associated with those concepts is reviewed in Table 9-1; Student's "t" values for use in the statistics of Table 9-1 appear in Table 9-2.

9.1.1.1 Regulatory and Scientific Objectives

The EPA, in its hazardous waste management system, has required that certain solid wastes be analyzed for physical and chemical properties. It is mostly chemical properties that are of concern, and, in the case of a number of chemical contaminants, the EPA has promulgated levels (regulatory thresholds) that cannot be equaled or exceeded. The regulations pertaining to the management of hazardous wastes contain three references regarding the

TABLE 9-1. BASIC STATISTICAL TERMINOLOGY APPLICABLE TO SAMPLING PLANS FOR SOLID WASTES

Terminology	Symbol	Mathematical equation	(Equation)
• Variable (e.g., barium or endrin)	x	—	
• Individual measurement of variable	x_i	—	
• Mean of all possible measurements of variable (population mean)	μ	$\mu = \frac{\sum_{i=1}^{N} x_i}{N}$, with N = number of possible measurements	(1)
• Mean of measurements generated by sample (sample mean)	$\bar{x}$	Simple random sampling and systematic random sampling: $\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$, with n = number of sample measurements	(2a)
		Stratified random sampling: $\bar{x} = \sum_{k=1}^{r} W_k \bar{x}_k$, with $\bar{x}_k$ = stratum mean and W_k = fraction of population represented by Stratum k (number of strata [k] range from 1 to r)	(2b)
• Variance of sample	s^2	Simple random sampling and systematic random sampling: $s^2 = \frac{\sum_{i=1}^{n} x_i^2 - (\sum_{i=1}^{n} x_i)^2/n}{n-1}$	(3a)
		Stratified random sampling: $s^2 = \sum_{k=1}^{r} W_k s_k^2$, with s_k^2 = stratum variance and W_k = fraction of population represent by Stratum k (number of strata [k] ranges from 1 to r)	(3b)

TABLE 9-1. (Continued)

Terminology	Symbol	Mathematical equation	(Equation)
• Standard deviation of sample	s	$s = \sqrt{s^2}$	(4)
• Standard error (also standard error of mean and standard deviation of mean) of sample	$s_{\bar{x}}$	$s_{\bar{x}} = \frac{s}{\sqrt{n}}$	(5)
• Confidence interval for μ[a]	CI	$CI = \bar{X} \pm t_{.20}\, s_{\bar{X}}$, with $t_{.20}$ obtained from Table 2 for appropriate degrees of freedom	(6)
• Regulatory threshold[a]	RT	Defined by EPA (e.g., 100 ppm for barium in elutriate of EP toxicity)	(7)
• Appropriate number of samples to collect from a solid waste (financial constraints not considered)	n	$n = \frac{t^2_{.20} s^2}{\Delta^2}$, with $\Delta = RT - \bar{x}$	(8)
• Degrees of freedom	df	$df = n - 1$	(9)
• Square root transformation	---	$X_i + 1/2$	(10)
• Arcsin transformation	---	Arcsin p; if necessary, refer to any text on basic statistics; measurements must be converted to percentages (p)	(11)

[a]The upper limit of the CI for μ is compared with the applicable regulatory threshold (RT) to determine if a solid waste contains the variable (chemical contaminant) of concern at a hazardous level. The contaminant of concern is not considered to be present in the waste at a hazardous level if the upper limit of the CI is less than the applicable RT. Otherwise, the opposite conclusion is reached.

TABLE 9-2. TABULATED VALUES OF STUDENT'S "t" FOR EVALUATING SOLID WASTES

Degrees of freedom (n-1)[a]	Tabulated "t" value[b]
1	3.078
2	1.886
3	1.638
4	1.533
5	1.476
6	1.440
7	1.415
8	1.397
9	1.393
10	1.372
11	1.363
12	1.356
13	1.350
14	1.345
15	1.341
16	1.337
17	1.333
18	1.330
19	1.328
20	1.325
21	1.323
22	1.321
23	1.319
24	1.318
25	1.316
26	1.315
27	1.314
28	1.313
29	1.311
30	1.310
40	1.303
60	1.296
120	1.289
	1.282

[a]Degrees of freedom (df) are equal to the number of samples (n) collected from a solid waste less one.

[b]Tabulated "t" values are for a two-tailed confidence interval and a probability of 0.20 (the same values are applicable to a one-tailed confidence interval and a probability of 0.10).

sampling of solid wastes for analytical properties. The first reference, which occurs throughout the regulations, requires that representative samples of waste be collected and defines representative samples as exhibiting average properties of the whole waste. The second reference, which pertains just to petitions to exclude wastes from being listed as hazardous wastes, specifies that enough samples (but in no case less than four samples) be collected over a period of time sufficient to represent the variability of the wastes. The third reference, which applies only to ground water monitoring systems, mandates that four replicates (subsamples) be taken from each ground water sample intended for chemical analysis and that the mean concentration and variance for each chemical constituent be calculated from those four subsamples and compared with background levels for ground water. Even the statistical test to be employed in that comparison is specified (Student's t-test).

The first of the above-described references addresses the issue of sampling accuracy, and the second and third references focus on sampling variability or, conversely, sampling precision (actually the third reference relates to analytical variability, which, in many statistical tests, is indistinguishable from true sampling variability). Sampling accuracy (the closeness of a sample value to its true value) and sampling precision (the closeness of repeated sample values) are also the issues of overriding importance in any scientific assessment of sampling practices. Thus, from both regulatory and scientific perspectives, the primary objectives of a sampling plan for a solid waste are twofold: namely, to collect samples that will allow measurements of the chemical properties of the waste that are both accurate and precise. If the chemical measurements are sufficiently accurate and precise, they will be considered reliable estimates of the chemical properties of the waste.

It is now apparent that a judgment must be made as to the degree of sampling accuracy and precision that is required to estimate reliably the chemical characteristics of a solid waste for the purpose of comparing those characteristics with applicable regulatory thresholds. Generally, high accuracy and high precision are required if one or more chemical contaminants of a solid waste are present at a concentration that is close to the applicable regulatory threshold. Alternatively, relatively low accuracy and low precision can be tolerated if the contaminants of concern occur at levels far below or far above their applicable thresholds. However, a word of caution is in order. Low sampling precision is often associated with considerable savings in analytical, as well as sampling, costs and is clearly recognizable even in the simplest of statistical tests. On the other hand, low sampling accuracy may not entail cost savings and is always obscured in statistical tests (i.e., it cannot be evaluated). Therefore, although it is desirable to design sampling plans for solid wastes to achieve only the minimally required precision (at least two samples of a material are required for any estimate of precision), it is prudent to design the plans to attain the greatest possible accuracy.

The roles that inaccurate and imprecise sampling can play in causing a solid waste to be inappropriately judged hazardous are illustrated in Figure 9-1. When evaluating Figure 9-1, several points are worthy of consideration. Although a sampling plan for a solid waste generates a mean concentration ($\bar{X}$) and standard deviation (s, a measure of the extent to which individual sample concentrations are dispersed around $\bar{X}$) for each chemical contaminant of concern, it is not the variation of individual sample concentrations that is of ultimate concern, but rather the variation that characterizes $\bar{X}$ itself. That measure of dispersion is termed the standard deviation of the mean (also, the standard error of the mean or standard error) and is designated as $s_{\bar{X}}$. Those two sample values, $\bar{X}$ and $s_{\bar{X}}$, are used to estimate the interval (range) within which the true mean (μ) of the chemical concentration probably occurs, under the assumption that the individual concentrations exhibit a normal (bell-shaped) distribution. For the purposes of evaluating solid wastes, the probability level (confidence interval) of 80% has been selected. That is, for each chemical contaminant of concern, a confidence interval (CI) is described within which μ occurs if the sample is representative, which is expected of about 80 out of 100 samples. The upper limit of the 80% CI is then compared with the appropriate regulatory threshold. If the upper limit is less than the threshold, the chemical contaminant is not considered to be present in the waste at a hazardous level; otherwise, the opposite conclusion is drawn. One last point merits explanation. Even if the upper limit of an estimated 80% CI is only slightly less than the regulatory threshold (the worst case of chemical contamination that would be judged acceptable), there is only a 10% (not 20%) chance that the threshold is equaled or exceeded. That is because values of a normally distributed contaminant that are outside the limits of an 80% CI are equally distributed between the left (lower) and right (upper) tails of the normal curve. Consequently, the CI employed to evaluate solid wastes is, for all practical purposes, a 90% interval.

9.1.1.2 Fundamental Statistical Concepts

The concepts of sampling accuracy and precision have already been introduced, along with some measurements of central tendency ($\bar{X}$) and dispersion (standard deviation [s] and $s_{\bar{X}}$) for concentrations of a chemical contaminant of a solid waste. The utility of $\bar{X}$ and $s_{\bar{X}}$ in estimating a confidence interval that probably contains the true mean (μ) concentration of a contaminant has also been described. However, it was noted that the validity of that estimate is predicated upon the assumption that individual concentrations of the contaminant exhibit a normal distribution.

Statistical techniques for obtaining accurate and precise samples are relatively simple and easy to implement. Sampling accuracy is usually achieved by some form of random sampling. In random sampling, every unit in the population (e.g., every location in a lagoon used to store a solid waste) has a theoretically equal chance of being sampled and measured. Consequently, statistics generated by the sample (e.g., $\bar{X}$ and, to a lesser degree, $s_{\bar{X}}$) are unbiased (accurate) estimators of true population parameters (e.g., the CI for μ). In other words, the sample is representative of the population. One of the commonest methods of selecting a random sample is to divide the

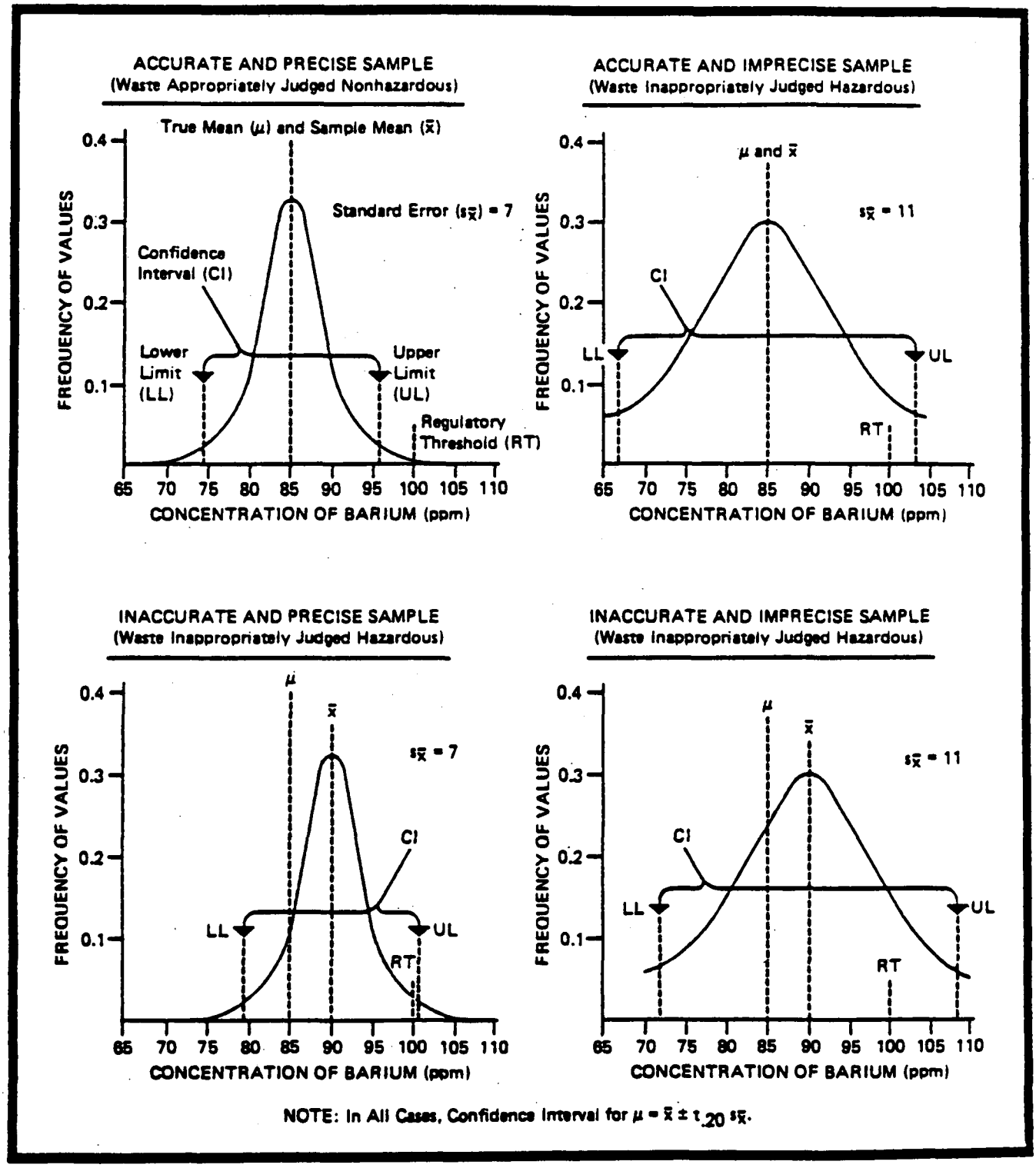


Figure 9-1.—Important theoretical relationships between sampling accuracy and precision and regulatory objectives for a chemical contaminant of a solid waste that occurs at a concentration marginally less than its regulatory threshold. In this example, barium is the chemical contaminant. The true mean concentration of barium in the elutriate of the EP toxicity test is 85 ppm, as compared to a regulatory threshold of 100 ppm. The upper limit of the confidence interval for the true mean concentration, which is estimated from the sample mean and standard error, must be less than the regulatory threshold if barium is judged to be present in the waste at a nonhazardous level.

population by an imaginary grid, assign a series of consecutive numbers to the units of the grid, and select the numbers (units) to be sampled through the use of a random-numbers table (such a table can be found in any text on basic statistics). It is important to emphasize that a haphazardly selected sample is not a suitable substitute for a randomly selected sample. That is because there is no assurance that a person performing undisciplined sampling will not consciously or subconsciously favor the selection of certain units of the population, thus causing the sample to be unrepresentative of the population.

Sampling precision is most commonly achieved by taking an appropriate number of samples from the population. As can be observed from the equation for calculating $s_{\bar{x}}$, precision increases ($s_{\bar{x}}$ and the CI for μ decrease) as the number of samples (n) increases, although not in a 1:1 ratio. For example, a 100% increase in the number of samples from two to four causes the CI to decrease by approximately 62% (about 31% of that decrease is associated with the critical upper tail of the normal curve). However, another 100% increase in sampling effort from four to eight samples results in only an additional 39% decrease in the CI. Another technique for increasing sampling precision is to maximize the physical size (weight or volume) of the samples that are collected. That has the effect of minimizing between-sample variation and, consequently, decreasing $s_{\bar{x}}$. Increasing the number or size of samples taken from a population, in addition to increasing sampling precision, has the secondary effect of increasing sampling accuracy.

In summary, reliable information concerning the chemical properties of a solid waste is needed for the purpose of comparing those properties with applicable regulatory thresholds. If chemical information is to be considered reliable, it must be accurate and sufficiently precise. Accuracy is usually achieved by incorporating some form of randomness into the selection process for the samples that generate the chemical information. Sufficient precision is most often obtained by selecting an appropriate number of samples.

There are a few ramifications of the above-described concepts that merit elaboration. If, for example, as in the case of semiconductor etching solutions, each batch of a waste is completely homogeneous with regard to the chemical properties of concern and that chemical homogeneity is constant (uniform) over time (from batch to batch), a single sample collected from the waste at an arbitrary location and time would theoretically generate an accurate and precise estimate of the chemical properties. However, most wastes are heterogeneous in terms of their chemical properties. If a batch of waste is randomly heterogeneous with regard to its chemical characteristics and that random chemical heterogeneity remains constant from batch to batch, accuracy and appropriate precision can usually be achieved by simple random sampling. In that type of sampling, all units in the population (essentially all locations or points in all batches of waste from which a sample could be collected) are identified, and a suitable number of samples is randomly selected from the population. More complex stratified random sampling is appropriate if a batch of waste is known to be nonrandomly heterogeneous in terms of its chemical properties and/or nonrandom chemical heterogeneity is known to exist from batch to batch. In such cases, the population is stratified to isolate the known sources of nonrandom chemical heterogeneity.

After stratification, which may occur over space (locations or points in a batch of waste) and/or time (each batch of waste), the units in each stratum are numerically identified, and a simple random sample is taken from each stratum. As previously intimated, both simple and stratified random sampling generate accurate estimates of the chemical properties of a solid waste. The advantage of stratified random sampling over simple random sampling is that, for a given number of samples and a given sample size, the former technique often results in a more precise estimate of chemical properties of a waste (a lower value of $s_{\bar{x}}$) than the latter technique. However, greater precision is likely to be realized only if a waste exhibits substantial nonrandom chemical heterogeneity and stratification efficiently "divides" the waste into strata that exhibit maximum between-strata variability and minimum within-strata variability. If that does not occur, stratified random sampling can produce results that are less precise than in the case of simple random sampling. Therefore, it is reasonable to select stratified random sampling over simple random sampling only if the distribution of chemical contaminants in a waste is sufficiently known to allow an intelligent identification of strata and at least two or three samples can be collected in each stratum. If a strategy employing stratified random sampling is selected, a decision must be made regarding the allocation of sampling effort among strata. When chemical variation within each stratum can be estimated with a great degree of detail, samples should be optimally allocated among strata, i.e., the number of samples collected from each stratum should be directly proportional to the chemical variation encountered in the stratum. When detailed information concerning chemical variability within strata is not available, samples should be proportionally allocated among strata, i.e., sampling effort in each stratum should be directly proportional to the size of the stratum.

Simple random sampling and stratified random sampling are types of probability sampling, which, because of a reliance upon mathematical and statistical theories, allows an evaluation of the effectiveness of sampling procedures. Another type of probability sampling is systematic random sampling, in which the first unit to be collected from a population is randomly selected, but all subsequent units are taken at fixed space or time intervals. An example of systematic random sampling is the sampling of a waste lagoon along a transect in which the first sampling point on the transect is 1 m from a randomly selected location on the shore and subsequent sampling points are located at 2-m intervals along the transect. The advantages of systematic random sampling over simple random sampling and stratified random sampling are the ease with which samples are identified and collected (the selection of the first sampling unit determines the remainder of the units) and, sometimes, an increase in precision. In certain cases, for example, systematic random sampling might be expected to be a little more precise than stratified random sampling with one unit per stratum because samples are distributed more evenly over the population. As will be demonstrated shortly, disadvantages of systematic random sampling are the poor accuracy and precision that can occur when unrecognized trends or cycles occur in the population. For those reasons, systematic random sampling is recommended only when a population is essentially random or contains at most a modest stratification. In such cases, systematic random sampling would be employed for the sake of convenience, with little expectation of an increase in precision over other random sampling techniques.

Probability sampling is contrasted with authoritative sampling, in which an individual who is well acquainted with the solid waste to be sampled selects a sample without regard to randomization. The validity of data gathered in that manner is totally dependent on the knowledge of the sampler and, although valid data can sometimes be obtained, authoritative sampling is not recommended for the chemical characterization of most wastes.

It may now be useful to offer a generalization regarding the four sampling strategies that have been identified for solid wastes. If little or no information is available concerning the distribution of chemical contaminants of a waste, simple random sampling is the most appropriate sampling strategy. As more information is accumulated for the contaminants of concern, greater consideration can be given (in order of the additional information required) to stratified random sampling, systematic random sampling, and, perhaps, authoritative sampling.

The validity of a CI for the true mean (μ) concentration of a chemical contaminant of a solid waste is, as previously noted, based on the assumption that individual concentrations of the contaminant exhibit a normal distribution. This is true regardless of the strategy that is employed to sample the waste. Although there are computational procedures for evaluating the correctness of the assumption of normality, those procedures are meaningful only if a large number of samples are collected from a waste. Because sampling plans for most solid wastes entail just a few samples, one can do little more than superficially examine resulting data for obvious departures from normality (this can be done by simple graphical methods), keeping in mind that even if individual measurements of a chemical contaminant of a waste exhibit a considerably abnormal distribution, such abnormality is not likely to be the case for sample means, which are our primary concern. One can also compare the mean of the sample ($\bar{x}$) with the variance of the sample (s^2). In a normally distributed population, $\bar{x}$ would be expected to be greater than s^2 (assuming that the number of samples [n] is reasonably large). If that is not the case, the chemical contaminant of concern may be characterized by a Poisson distribution ($\bar{x}$ is approximately equal to s^2) or a negative binomial distribution ($\bar{x}$ is less than s^2). In the former circumstance, normality can often be achieved by transforming data according to the square root transformation. In the latter circumstance, normality may be realized through use of the arcsine transformation. If either transformation is required, all subsequent statistical evaluations must be performed on the transformed scale.

Finally, it is necessary to address the appropriate number of samples to be employed in the chemical characterization of a solid waste. As has already been emphasized, the appropriate number of samples is the least number of samples required to generate a sufficiently precise estimate of the true mean (μ) concentration of a chemical contaminant of a waste. From the perspective of most waste producers, that means the minimal number of samples needed to demonstrate that the upper limit of the CI for μ is less than the applicable regulatory threshold (RT). The formula for estimating appropriate sampling effort (Table 9-1, Equation 8) indicates that increased sampling effort is generally justified as s^2 or the "$t_{.20}$" value (probable error rate) increases

and as $\Delta(RT - \bar{X})$ decreases. In a well-designed sampling plan for a solid waste, an effort is made to estimate the values of $\bar{X}$ and s^2 before sampling is initiated. Such preliminary estimates, which may be derived from information pertaining to similar wastes, process engineering data, or limited analytical studies, are used to identify the approximate number of samples that must be collected from the waste. It is always prudent to collect a somewhat greater number of samples than indicated by preliminary estimates of $\bar{X}$ and s^2 since poor preliminary estimates of those statistics can result in an underestimate of the appropriate number of samples to collect. It is usually possible to process and store the extra samples appropriately until analysis of the initially identified samples is completed and it can be determined if analysis of the additional samples is warranted.

9.1.1.3 Basic Sampling Strategies

It is now appropriate to present general procedures for implementing the three previously introduced sampling strategies (simple random sampling, stratified random sampling, and systematic random sampling) and a hypothetical example of each sampling strategy. The hypothetical examples illustrate the statistical calculations that must be performed in most situations likely to be encountered by a waste producer and, also, provide some insight into the efficiency of the three sampling strategies in meeting regulatory objectives.

The following hypothetical conditions are assumed to exist for all three sampling strategies. First, barium, which has an RT of 100 ppm as measured in the EP elutriate test, is the only chemical contaminant of concern. Second, barium is discharged in particulate form to a waste lagoon and accumulates in the lagoon in the form of a sludge, which has built up to approximately the same thickness throughout the lagoon. Third, concentrations of barium are relatively homogeneous along the vertical gradient (from the water-sludge interface to the sludge-lagoon interface), suggesting a highly controlled manufacturing process (little between-batch variation in barium concentrations). Fourth, the physical size of sludge samples collected from the lagoon is as large as practical, and barium concentrations derived from those samples are normally distributed (note that we do not refer to barium levels in the samples of sludge because barium measurements are actually made on the elutriate from EP toxicity tests performed with the samples). Last, a preliminary study of barium levels in the elutriate of four EP toxicity tests conducted with sludge collected from the lagoon several years ago identified values of 86 and 90 ppm for material collected near the outfall (in the upper third) of the lagoon and values of 98 and 104 ppm for material obtained from the far end (the lower two-thirds) of the lagoon.

For all sampling strategies, it is important to remember that barium will be determined to be present in the sludge at a hazardous level if the upper limit of the CI for μ is equal to or greater than the RT of 100 ppm (Table 9-1, Equations 6 and 7).

9.1.1.3.1 Simple Random Sampling

Simple random sampling (Box 1) is performed by general procedures in which preliminary estimates of $\bar{x}$ and s^2, as well as a knowledge of the RT, for each chemical contaminant of a solid waste that is of concern are employed to estimate the appropriate number of samples (n) to be collected from the waste. That number of samples is subsequently analyzed for each chemical contaminant of concern. The resulting analytical data are then used to conclude definitively that each contaminant is or is not present in the waste at a hazardous concentration or, alternatively, to suggest a reiterative process, involving increased sampling effort, through which the presence or absence of hazard can be definitively determined.

In the hypothetical example for simple random sampling (Box 1), preliminary estimates of $\bar{x}$ and s^2 indicated a sampling effort consisting of six samples. That number of samples was collected and initially analyzed, generating analytical data somewhat different from the preliminary data (s^2 was substantially greater than was preliminarily estimated). Consequently, the upper limit of the CI was unexpectedly greater than the applicable RT, resulting in a tentative conclusion of hazard. However, a reestimation of appropriate sampling effort, based on statistics derived from the six samples, suggested that such a conclusion might be reversed through the collection and analysis of just one more sample. Fortunately, a resampling effort was not required because of the foresight of the waste producer in obtaining three extra samples during the initial sampling effort, which, because of their influence in decreasing the final values of $\bar{x}$, $s_{\bar{x}}$, $t_{.20}$, and, consequently, the upper limit of the CI -- values obtained from all nine samples -- resulted in a definitive conclusion of nonhazard.

9.1.1.3.2 Stratified Random Sampling

Stratified random sampling (Box 2) is conducted by general procedures that are similar to the procedures described for simple random sampling. The only difference is that, in stratified random sampling, values of $\bar{x}$ and s^2 are calculated for each stratum in the population and then integrated into overall estimates of those statistics, the standard deviation (s), $s_{\bar{x}}$, and the appropriate number of samples (n) for all strata.

The hypothetical example for stratified random sampling (Box 2) is based on the same nine sludge samples previously identified in the example of simple random sampling (Box 1) so that the relative efficiencies of the two sampling strategies can be fully compared. The efficiency generated through the process of stratification is first evident in the preliminary estimate of n (Step 2 in Boxes 1 and 2), which is six for simple random sampling and four for stratified random sampling. (The lesser value for stratified sampling is the consequence of a dramatic decrease in s^2, which more than compensated for a modest increase in Δ.) The most relevant indication of sampling efficiency is the value of $s_{\bar{x}}$, which is directly employed to calculate the CI. In the case of simple random sampling, $s_{\bar{x}}$ is calculated as 2.58 (Step 9 in Box 1), and, for stratified random sampling, $s_{\bar{x}}$ is determined to be 2.35 (Steps 5 and 7 in Box 2). Consequently, the gain in efficiency attributable to stratification is approximately 9% (0.23/2.58).

BOX 1. STRATEGY FOR DETERMINING IF CHEMICAL CONTAMINANTS OF SOLID WASTES ARE PRESENT AT HAZARDOUS LEVELS - SIMPLE RANDOM SAMPLING

Step	General Procedures

1. Obtain preliminary estimates of $\bar{x}$ and s^2 for each chemical contaminant of a solid waste that is of concern. The two above-identified statistics are calculated by, respectively, Equations 2a and 3a (Table 9-1).

2. Estimate the appropriate number of samples (n_1) to be collected from the waste through use of Equation 8 (Table 9-1) and Table 9-2. Derive individual values of n_1 for each chemical contaminant of concern. The appropriate number of samples to be taken from the waste is the greatest of the individual n_1 values.

3. Randomly collect at least n_1 (or $n_2 - n_1$, $n_3 - n_2$, etc., as will be indicated later in this box) samples from the waste (collection of a few extra samples will provide protection against poor preliminary estimates of $\bar{x}$ and s^2). Maximize the physical size (weight or volume) of all samples that are collected.

4. Analyze the n_1 (or $n_2 - n_1$, $n_3 - n_2$ etc.) samples for each chemical contaminant of concern. Superficially (graphically) examine each set of analytical data for obvious departures from normality.

5. Calculate $\bar{x}$, s^2, the standard deviation (s), and $s_{\bar{x}}$ for each set of analytical data by, respectively, Equations 2a, 3a, 4, and 5 (Table 9-1).

6. If $\bar{x}$ for a chemical contaminant is equal to or greater than the applicable RT (Equation 7, Table 9-1) and is believed to be an accurate estimator of μ, the contaminant is considered to be present in the waste at a hazardous concentration, and the study is completed. Otherwise, continue the study. In the case of a set of analytical data that does not exhibit obvious abnormality and for which $\bar{x}$ is greater than s^2, perform the following calculations with nontransformed data. Otherwise, consider transforming the data by the square root transformation (if $\bar{x}$ is about equal to s^2) or the arcsine transformation (if $\bar{x}$ is less than s^2) and performing all subsequent calculations with transformed data. Square root and arcsine transformations are defined by, respectively, Equations 10 and 11 (Table 9-1).

7. Determine the CI for each chemical contaminant of concern by Equation 6 (Table 9-1) and Table 9-2. If the upper limit of the CI is less than the applicable RT (Equations 6 and 7, Table 9-1), the chemical contaminant is not considered to be present in the waste at a hazardous concentration and the study is completed. Otherwise, the opposite conclusion is tentatively reached.

8. If a tentative conclusion of hazard is reached, reestimate the total number of samples (n_2) to be collected from the waste by use of Equation 8 (Table 9-1) and Table 9-2. When deriving n_2, employ the newly calculated (not preliminary) values of x and s^2. If additional $n_2 - n_1$ samples of waste cannot reasonably be collected, the study is completed, and a definitive conclusion of hazard is reached. Otherwise, collect extra $n_2 - n_1$ samples of waste.

9. Repeat the basic operations described in Steps 3 through 8 until the waste is judged to be nonhazardous or, if the opposite conclusion continues to be reached, until increased sampling effort is impractical.

Hypothetical Example

Step

1. The preliminary study of barium levels in the elutriate of four EP toxicity tests, conducted with sludge collected from the lagoon several years ago, generated values of 86 and 90 ppm for sludge obtained from the upper third of the lagoon and values of 98 and 104 ppm for sludge from the lower two-thirds of the lagoon. Those two sets of values are not judged to be indicative of nonrandom chemical heterogeneity (stratification) within the lagoon. Therefore, preliminary estimates of $\bar{x}$ and s^2 are calculated as:

$$\bar{x} = \frac{\sum_{i=1}^{n} X_i}{n} = \frac{86 + 90 + 98 + 104}{4} = 94.50, \text{ and} \qquad \text{(Equation 2a)}$$

$$s^2 = \frac{\sum_{i=1}^{n} X_i^2 - \left(\sum_{i=1}^{n} X_i\right)^2/n}{n - 1} \qquad \text{(Equation 3a)}$$

$$= \frac{35{,}916.00 - 35{,}721.00}{3} = 65.00.$$

2. Based on the preliminary estimates of $\bar{x}$ and s^2, as well as the knowledge that the RT for barium is 100 ppm,

$$n_1 = \frac{t^2_{.20} s^2}{\Delta^2} = \frac{(1.638^2)(65.00)}{5.50^2} = 5.77. \qquad \text{(Equation 8)}$$

3. As indicated above, the appropriate number of sludge samples (n_1) to be collected from the lagoon is six. That number of samples (plus three extra samples for protection against poor preliminary estimates of $\bar{x}$ and s^2) is collected from the lagoon by a single randomization process (Figure 9-2). All samples consist of the greatest volume of sludge that

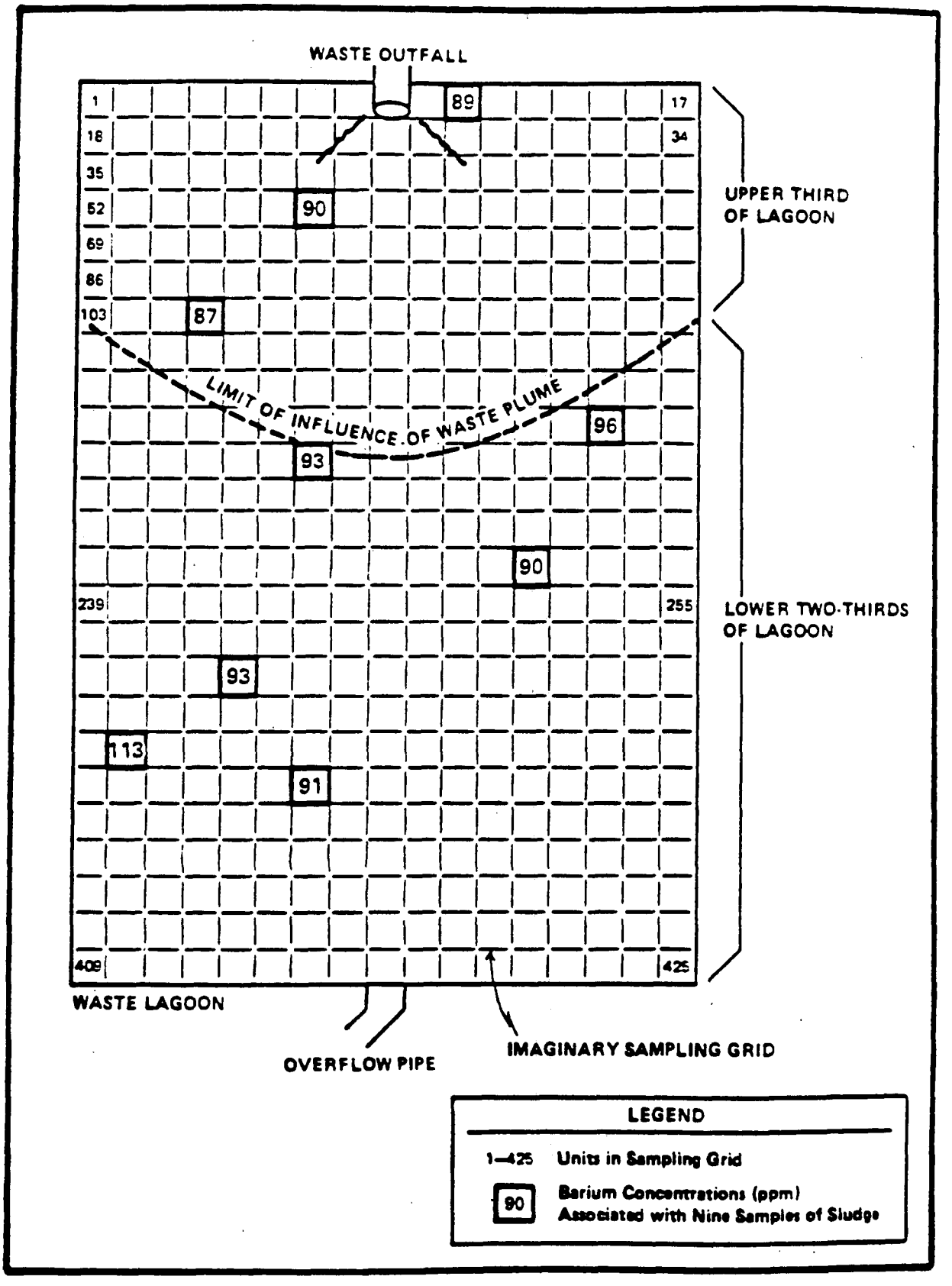


Figure 9-2.—Hypothetical sampling conditions in waste lagoon containing sludge contaminated with barium. Barium concentrations associated with samples of sludge refer to levels measured in the elutriate of EP toxicity tests conducted with the samples.

can be practically collected. The three extra samples are suitably processed and stored for possible later analysis.

4. The six samples of sludge (n_1) designated for immediate analysis generate the following concentrations of barium in the EP toxicity test: 89, 90, 87, 96, 93, and 113 ppm. Although the value of 113 ppm appears unusual as compared with the other data, there is no obvious indication that the data are not normally distributed.

5. New values for $\bar{x}$ and s^2 and associated values for the standard deviation (s) and $s_{\bar{x}}$ are calculated as:

$$\bar{x} = \frac{\sum_{i=1}^{n} X_i}{n} = \frac{89 + 90 + 87 + 96 + 93 + 113}{6} = 94.67, \qquad \text{(Equation 2a)}$$

$$s^2 = \frac{\sum_{i=1}^{n} X_i^2 - \left(\sum_{i=1}^{n} X_i\right)^2/n}{n - 1} \qquad \text{(Equation 3a)}$$

$$= \frac{54,224.00 - 53,770.67}{5} = 90.67,$$

$$s = \sqrt{s^2} = 9.52, \text{ and} \qquad \text{(Equation 4)}$$

$$s_{\bar{x}} = s/\sqrt{n} = 9.52/\sqrt{6} = 3.89. \qquad \text{(Equation 5)}$$

6. The new value for $\bar{x}$ (94.67) is less than the RT (100). In addition, $\bar{x}$ is greater (only slightly) than s^2 (90.67), and, as previously indicated, the raw data are not characterized by obvious abnormality. Consequently, the study is continued, with the following calculations performed with nontransformed data.

7. $$CI = \bar{x} \pm t_{.20} s_{\bar{x}} = 94.67 \pm (1.476)(3.89) \qquad \text{(Equation 6)}$$

$$= 94.67 \pm 5.74.$$

Because the upper limit of the CI (100.41) is greater than the applicable RT (100), it is tentatively concluded that barium is present in the sludge at a hazardous concentration.

8. n is now reestimated as:

$$n_2 = \frac{t^2_{.20} s^2}{\Delta^2} \frac{(1.476^2)(90.67)}{5.33^2} = 6.95. \qquad \text{(Equation 8)}$$

The value for n_2 (approximately 7) indicates that an additional ($n_2 - n_1 = 1$) sludge sample should be collected from the lagoon.

9. The additional sampling effort is not necessary because of the three extra samples that were initially collected from the lagoon. All extra samples are analyzed, generating the following levels of barium for the EP toxicity test: 93, 90, and 91 ppm. Consequently, $\bar{x}$, s^2, the standard deviation (s), and $s_{\bar{x}}$ are recalculated as:

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n} = \frac{86 + 90 + \ldots + 91}{9} = 93.56\ , \qquad \text{(Equation 2a)}$$

$$s^2 = \frac{\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2/n}{n - 1} \qquad \text{(Equation 3a)}$$

$$= \frac{79{,}254.00 - 78{,}773.78}{8} = 60.03,$$

$$s = \sqrt{s^2} = 7.75, \text{ and} \qquad \text{(Equation 4)}$$

$$s_{\bar{x}} = s/\sqrt{n} = 7.75/\sqrt{9} = 2.58. \qquad \text{(Equation 5)}$$

The value for $\bar{x}$ (93.56) is again less than the RT (100), and there is no indication that the nine data points, considered collectively, are abnormally distributed (in particular, $\bar{x}$ is now substantially greater than s^2). Consequently, CI, calculated with nontransformed data, is determined to be:

$$CI = \bar{x} \pm t_{.20} s_{\bar{x}} = 93.56 \pm (1.397)(2.58) \qquad \text{(Equation 6)}$$

$$= 93.56 \pm 3.60.$$

The upper limit of the CI (97.16) is now less than the RT of 100. Consequently, it is definitively concluded that barium is not present in the sludge at a hazardous level.

BOX 2. STRATEGY FOR DETERMINING IF CHEMICAL CONTAMINANTS OF SOLID WASTES ARE PRESENT AT HAZARDOUS LEVELS - STRATIFIED RANDOM SAMPLING

Step	General Procedures

1. Obtain preliminary estimates of $\bar{x}$ and s^2 for each chemical contaminant of a solid waste that is of concern. The two above-identified statistics are calculated by, respectively, Equations 2b and 3b (Table 9-1).

2. Estimate the appropriate number of samples (n_1) to be collected from the waste through use of Equation 8 (Table 9-1) and Table 9-2. Derive individual values of n_1 for each chemical contaminant of concern. The appropriate number of samples to be taken from the waste is the greatest of the individual n_1 values.

3. Randomly collect at least n_1 (or $n_2 - n_1$, $n_3 - n_2$, etc., as will be indicated later in this box) samples from the waste (collection of a few extra samples will provide protection against poor preliminary estimates of $\bar{x}$ and s^2). If s_k for each stratum (see Equation 3b) is believed to be an accurate estimate, optimally allocate samples among strata (i.e., allocate samples among strata so that the number of samples collected from each stratum is directly proportional to s_k for that stratum). Otherwise, proportionally allocate samples among strata according to size of the strata. Maximize the physical size (weight or volume) of all samples that are collected from the strata.

4. Analyze the n_1 (or $n_2 - n_1$, $n_3 - n_2$ etc.) samples for each chemical contaminant of concern. Superficially (graphically) examine each set of analytical data from each stratum for obvious departures from normality.

5. Calculate $\bar{x}$, s_2, the standard deviation (s), and $s_{\bar{x}}$ for each set of analytical data by, respectively, Equations 2b, 3b, 4, and 5 (Table 9-1).

6. If $\bar{x}$ for a chemical contaminant is equal to or greater than the applicable RT (Equation 7, Table 9-1) and is believed to be an accurate estimator of u, the contaminant is considered to be present in the waste at a hazardous concentration, and the study is completed. Otherwise, continue the study. In the case of a set of analytical data that does not exhibit obvious abnormality and for which $\bar{x}$ is greater than s^2, perform the following calculations with nontransformed data. Otherwise, consider transforming the data by the square root transformation (if $\bar{x}$ is about equal to s^2) or the arcsine transformation (if $\bar{x}$ is less than s^2) and performing all subsequent calculations with transformed data. Square root and arcsine transformations are defined by, respectively, Equations 10 and 11 (Table 9-1).

7. Determine the CI for each chemical contaminant of concern by Equation 6 (Table 9-1) and Table 9-2. If the upper limit of the CI is less than the applicable RT (Equations 6 and 7, Table 9-1), the chemical contaminant is not considered to be present in the waste at a hazardous concentration, and the study is completed. Otherwise, the opposite conclusion is tentatively reached.

8. If a tentative conclusion of hazard is reached, reestimate the total number of samples (n_2) to be collected from the waste by use of Equation 8 (Table 9-1) and Table 9-2. When deriving n_2, employ the newly calculated (not preliminary) values of $\bar{x}$ and s^2. If additional $n_2 - n_1$ samples of waste cannot reasonably be collected, the study is completed, and a definitive conclusion of hazard is reached. Otherwise, collect extra $n_2 - n_1$ samples of waste.

9. Repeat the basic operations described in steps 3 through 8 until the waste is judged to be nonhazardous or, if the opposite conclusion continues to be reached, until increased sampling effort is impractical.

Hypothetical Example

Step

1. The preliminary study of barium levels in the elutriate of four EP toxicity tests, conducted with sludge collected from the lagoon several years ago, generated values of 86 and 90 ppm for sludge obtained from the upper third of the lagoon and values of 98 and 104 ppm for sludge from the lower two-thirds of the lagoon. Those two sets of values are not judged to be indicative of nonrandom chemical heterogeneity (stratification) within the lagoon. Therefore, preliminary estimates of $\bar{x}$ and s^2 are calculated as:

$$\bar{x} = \sum_{k=1}^{r} W_k \bar{x}_k = \frac{(1)(88.00)}{3} + \frac{(2)(101.00)}{3} = 96.67, \text{ and} \qquad \text{(Equation 2b)}$$

$$s^2 = \sum_{k=1}^{r} W_k s_k^2 = \frac{(1)(8.00)}{3} + \frac{(2)(18.00)}{3} = 14.67. \qquad \text{(Equation 3b)}$$

2. Based on the preliminary estimates of $\bar{x}$ and s^2, as well as the knowledge that the RT for barium is 100 ppm,

$$n_1 = \frac{t^2_{.20} s^2}{\Delta^2} = \frac{(1.368^2)(14.67)}{3.33^2} = 3.55. \qquad \text{(Equation 8)}$$

3. As indicated above, the appropriate number of sludge samples (n_1) to be collected from the lagoon is four. However, for purposes of comparison with simple random sampling (Box 1), six samples (plus three extra samples for protection against poor preliminary estimates of $\bar{x}$ and s^2) are collected from the lagoon by a two-stage randomization process (Figure 2). Because s_k for the upper (2.12 ppm) and lower (5.66 ppm) strata are not believed to be very accurate estimates, the nine samples to be collected from the lagoon are not optimally allocated between the two strata (optimum allocation would require two and seven samples to be

collected from the upper and lower strata, respectively). Alternatively, proportional allocation is employed: three samples are collected from the upper stratum (which represents one-third of the lagoon), and six samples are taken from the lower stratum (two-thirds of the lagoon). All samples consist of the greatest volume of sludge that can be practically collected.

4. The nine samples of sludge generate the following concentrations of barium in the EP toxicity test: upper stratum -- 89, 90, and 87 ppm; lower stratum -- 96, 93, 113, 93, 90, and 91 ppm. Although the value of 113 ppm appears unusual as compared with the other data for the lower stratum, there is no obvious indication that the data are not normally distributed.

5. New values for $\bar{x}$ and s^2 and associated values for the standard deviation (s) and $s_{\bar{x}}$ are calculated as:

$$\bar{x} = \sum_{k=1}^{r} W_k \bar{x}_k = \frac{(1)(88.67)}{3} + \frac{(2)(96.00)}{3} = 93.56, \qquad \text{(Equation 2b)}$$

$$s^2 = \sum_{k=1}^{r} W_k s_k^2 = \frac{(1)(2.33)}{3} + \frac{(2)(73.60)}{3} = 49.84, \qquad \text{(Equation 3b)}$$

$$s = \sqrt{s^2} = 7.06, \text{ and} \qquad \text{(Equation 4)}$$

$$s_{\bar{x}} = s/\sqrt{n} = 7.06/\sqrt{9} = 2.35. \qquad \text{(Equation 5)}$$

6. The new value for $\bar{x}$ (93.56) is less than the RT (100). In addition, $\bar{x}$ is greater than s^2 (49.84), and, as previously indicated, the raw data are not characterized by obvious abnormality. Consequently, the study is continued, with the following calculations performed with nontransformed data.

7. $$CI = \bar{x} \pm t_{.20} s_{\bar{x}} = 93.56 \pm (1.397)(2.35) \qquad \text{(Equation 6)}$$

$$= 93.56 \pm 3.28$$

The upper limit of the CI (96.84) is less than the applicable RT (100). Therefore, it is concluded that barium is not present in the sludge at a hazardous concentration.

9.1.1.3.3 Systematic Random Sampling

Systematic random sampling (Box 3) is implemented by general procedures that are identical to the procedures identified for simple random sampling. The hypothetical example for systematic random sampling (Box 3) demonstrates the bias and imprecision that are associated with that type of sampling when unrecognized trends or cycles exist in the population.

9.1.1.4 Special Considerations

The preceding discussion has addressed the major issues that are critical to the development of a reliable sampling strategy for a solid waste. The remaining discussion focuses on several "secondary" issues that should be considered when designing an appropriate sampling strategy. These secondary issues are applicable to all three of the basic sampling strategies that have been identified.

9.1.1.4.1 Composite Sampling

In composite sampling, a number of random samples are initially collected from a waste and combined into a single sample, which is then analyzed for the chemical contaminants of concern. The major disadvantage of composite sampling, as compared with noncomposite sampling, is that information concerning the chemical contaminants is lost, i.e., each initial set of samples generates only a single estimate of the concentration of each contaminant. Consequently, because the number of analytical measurements (n) is small, $s_{\bar{x}}$ and $t_{.20}$ are large, thus decreasing the likelihood that a contaminant will be judged to occur in the waste at a nonhazardous level (refer to appropriate equations in Table 9-1 and to Table 9-2). A remedy to that situation is to collect and analyze a relatively large number of composite samples, thereby offsetting the savings in analytical costs that are often associated with composite sampling, but achieving better representation of the waste than would occur with noncomposite sampling.

The appropriate number of composite samples to be collected from a solid waste is estimated by use of Equation 8 (Table 9-1), as previously described for the three basic sampling strategies. In comparison with noncomposite sampling, composite sampling may have the effect of minimizing between-sample variation (the same phenomenon that occurs when the physical size of a sample is maximized), thereby reducing somewhat the number of samples that must be collected from the waste.

9.1.1.4.2 Subsampling

The variance (s^2) associated with a chemical contaminant of a waste consists of two components in that:

$$s^2 = s_s^2 + \frac{s_a^2}{m}, \qquad \text{(Equation 12)}$$

BOX 3. STRATEGY FOR DETERMINING IF CHEMICAL CONTAMINANTS OF SOLID WASTES ARE PRESENT AT HAZARDOUS LEVELS - SYSTEMATIC RANDOM SAMPLING

Step	General Procedures
1.	Follow general procedures presented for simple random sampling of solid wastes (Box 1).

Step	Hypothetical Example
1.	The example presented in Box 1 is applicable to systematic random sampling, with the understanding that the nine sludge samples obtained from the lagoon would be collected at equal intervals along a transect running from a randomly selected location on one bank of the lagoon to the opposite bank. If that randomly selected transect were established between Units 1 and 409 of the sampling grid (Figure 9-2) and sampling were performed at Unit 1 and thereafter at three-unit intervals along the transect (i.e., Unit 1, Unit 52, Unit 103, ... , and Unit 409), it is apparent that only two samples would be collected in the upper third of the lagoon, whereas seven samples would be obtained from the lower two-thirds of the lagoon. If, as suggested by the barium concentrations illustrated in Figure 9-2, the lower part of the lagoon is characterized by greater and more variable barium contamination than the upper part of the lagoon, systematic random sampling along the above-identified transect, by placing undue (disproportionate) emphasis on the lower part of the lagoon, might be expected to result in an inaccurate (overestimated) and imprecise characterization of barium levels in the whole lagoon, as compared with either simple random sampling or stratified random sampling. Such inaccuracy and imprecision, which are typical of systematic random sampling when unrecognized trends or cycles occur in the population, would be magnified if, for example, the randomly selected transect were established solely in the lower part of the lagoon, e.g., between Units 239 and 255 of the sampling grid.

where s_s^2 = a component attributable to sampling (sample) variation, s_a^2 = a component attributable to analytical (subsample) variation, and m = number of subsamples. In general, s_a^2 should not be allowed to exceed one-ninth of s_s^2. If a preliminary study indicates that s_a^2 exceeds that threshold, a sampling strategy involving subsampling should be considered. In such a strategy, a number of replicate measurements are randomly made on a relatively limited number of randomly collected samples. Consequently, analytical effort is allocated as a function of analytical variability. The efficiency of that general strategy in meeting regulatory objectives has already been demonstrated in the previous discussions of sampling effort.

The appropriate number of samples (n) to be collected from a solid waste for which subsampling will be employed is again estimated by Equation 8 (Table 9-1). In the case of simple random sampling or systematic random sampling with an equal number of subsamples analyzed per sample:

$$\bar{x} = \sum_{i=1}^{n} x_i/n, \qquad \text{(Equation 13)}$$

where $\bar{x}_i$ = sample mean (calculated from values for subsamples) and n = number of samples. Also,

$$s^2 = \frac{\sum_{i=1}^{n} \bar{x}_i^2 - \left(\sum_{i=1}^{n} \bar{x}_i\right)^2/n}{n - 1} \qquad \text{(Equation 14)}$$

The optimum number of subsamples to be taken from each sample ($m_{opt.}$) is estimated as:

$$m_{(opt.)} = \frac{s_a}{s_s} \qquad \text{(Equation 15)}$$

when cost factors are not considered. The value for s_a is calculated from available data as:

$$s_a = \sqrt{\frac{\sum_{i=1}^{n}\sum_{j=1}^{m} x_{ij}^2 - \left(\sum x_{ij}\right)^2/m}{n\,(m - 1)}}, \qquad \text{(Equation 16)}$$

and s_s, which can have a negative characteristic, is defined as:

$$s_s = \sqrt{s^2 - \frac{s_a^2}{m}}, \qquad \text{(Equation 17)}$$

with s_2 calculated as indicated in Equation 14.

In the case of stratified random sampling with subsampling, critical formulas for estimating sample size (n) by Equation 8 (Table 9-1) include:

$$\bar{x} = \sum_{k=1}^{r} W_k \bar{x}_k, \qquad \text{(Equation 2b)}$$

where $\bar{x}_k$ = stratum mean and W_k = fraction of population represented by Stratum K (number of strata, k, ranges from 1 to r). In Equation 2b, $\bar{x}_k$ for each stratum is calculated as the average of all sample means in the stratum (sample means are calculated from values for subsamples). In addition, s^2 is calculated by:

$$s^2 = \sum_{k=1}^{r} W_k s_k^2, \qquad \text{(Equation 3b)}$$

with s^2_k for each stratum calculated from all sample means in the stratum. The optimum subsampling effort when cost factors are not considered and all replication is symmetrical is again estimated as:

$$m_{(opt.)} = \frac{s_a}{s_s}, \text{ with} \qquad \text{(Equation 15)}$$

$$s_a = \sqrt{\frac{\sum_{k=1}^{r}\sum_{i=1}^{n}\sum_{j=1}^{m} x_{kij}^2 - (\sum x_{kij})^2/m}{rn\,(m-1)}}, \text{ and} \qquad \text{(Equation 18)}$$

$$s_s = \sqrt{s^2 - \frac{s_a^2}{m}}, \qquad \text{(Equation 17)}$$

with s^2 derived as shown in Equation 3b.

9.1.1.5 Cost and Loss Functions

The cost of chemically characterizing a waste is dependent on the specific strategy that is employed to sample the waste. For example, in the case of simple random sampling without subsampling, a reasonable cost function might be:

$$C_{(n)} = C_0 + C_1 n, \qquad \text{(Equation 19)}$$

where $C_{(n)}$ = cost of employing a sample size of n, C_0 = an overhead cost (which is independent of the number of samples that are collected and analyzed), and C_1 = a sample-dependent cost. A consideration of $C_{(n)}$ mandates an evaluation of $L_{(n)}$, which is the sample-size-dependent expected financial loss related to the erroneous conclusion that a waste is hazardous. A simple loss function is:

$$L_{(n)} = \frac{\alpha s^2}{n} \quad , \qquad \text{(Equation 20)}$$

with α = a constant related to the cost of a waste management program if the waste is judged to be hazardous, s^2 = sample variance, and n = number of samples. A primary objective of any sampling strategy is to minimize $C_{(n)} + L_{(n)}$. Differentiation of Equations 19 and 20 indicates that the number of samples (n) that minimize $C_{(n)} + L_{(n)}$ is:

$$n = \sqrt{\frac{\alpha s^2}{C_1}} \quad . \qquad \text{(Equation 21)}$$

As is evident from Equation 21, a comparatively large number of samples (n) is justified if the value of α or s^2 is large, whereas a relatively small number of samples is appropriate if the value of C_1 is large. These general conclusions are valid for any sampling strategy for a solid waste.

9.2 IMPLEMENTATION

This section discusses the implementation of a sampling plan for the collection of a "solid waste," as defined by Section 261.2 of the Resource Conservation and Recovery Act (RCRA) regulations. Due to the uniqueness of each sampling effort, the following discussion is in the general form of guidance which, when applied to each sampling effort, should improve and document the quality of the sampling and the representativeness of samples.

The following subsections address elements of a sampling effort in a logical order, from defining objectives through compositing samples prior to analysis.

9.2.1 Definition Of Objectives

After verifying the need for sampling, those personnel directing the sampling effort should define the program's objectives. The need for a sampling effort should not be confused with the objective. When management, a regulation, or a regulatory agency requires sampling, the need for sampling is established but the objectives must be defined.

The primary objective of any waste sampling effort is to obtain information that can be used to evaluate a waste. It is essential that the specific information needed and its uses are defined in detail at this stage. The information needed is usually more complex than just a concentration of a specified parameter; it may be further qualified (e.g., by sampling location or sampling time.) The manner in which the information is to be used can also have a substantial impact on the design of a sampling plan. (Are the data to be used in a qualitative or quantitative manner? If quantitative, what are the accuracy and precision requirements?)

All pertinent information should be gathered. For example, if the primary objective has been roughly defined as "collecting samples of waste which will be analyzed to comply with environmental regulations," then ask the following questions:

1. The sampling is being done to comply with which evironmental regulation? Certain regulations detail specific or minimum protocols (e.g., exclusion petitions as defined in §260.22 of the RCRA regulations); the sampling effort must comply with these regulatory requirements.

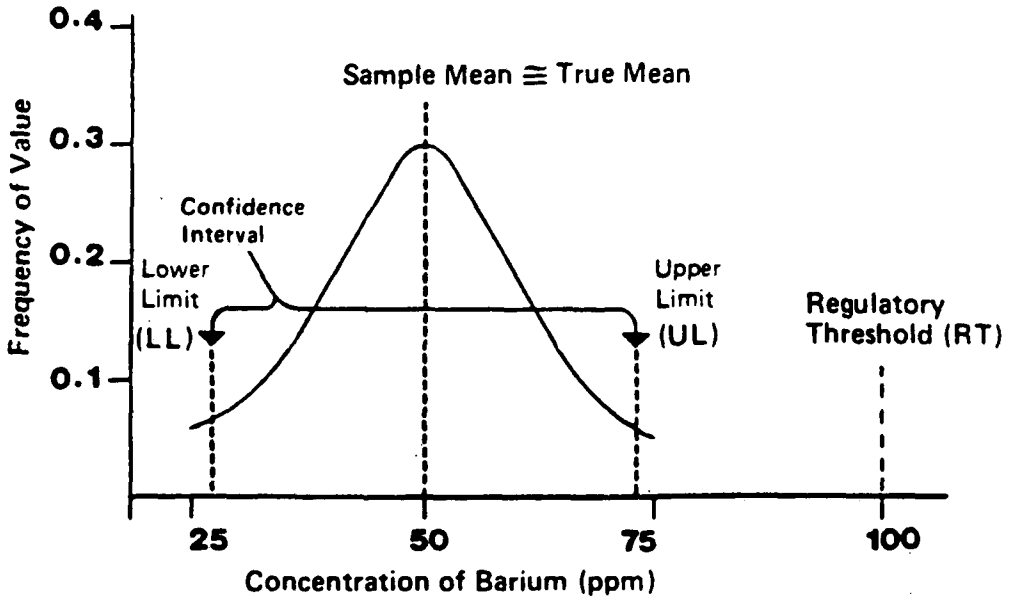
2. The collected samples are to be analyzed for which parameters? Why those and not others? Should the samples be analyzed for more or fewer parameters?

3. What waste is to be sampled: the waste as generated? the waste prior to or after mixing with other wastes or stabilizing agents? the waste after aging or drying or just prior to disposal? Should waste disposed of 10 years ago be sampled to acquire historical data?

4. What is the end-use of the generated data base? What are the required degrees of accuracy and precision?

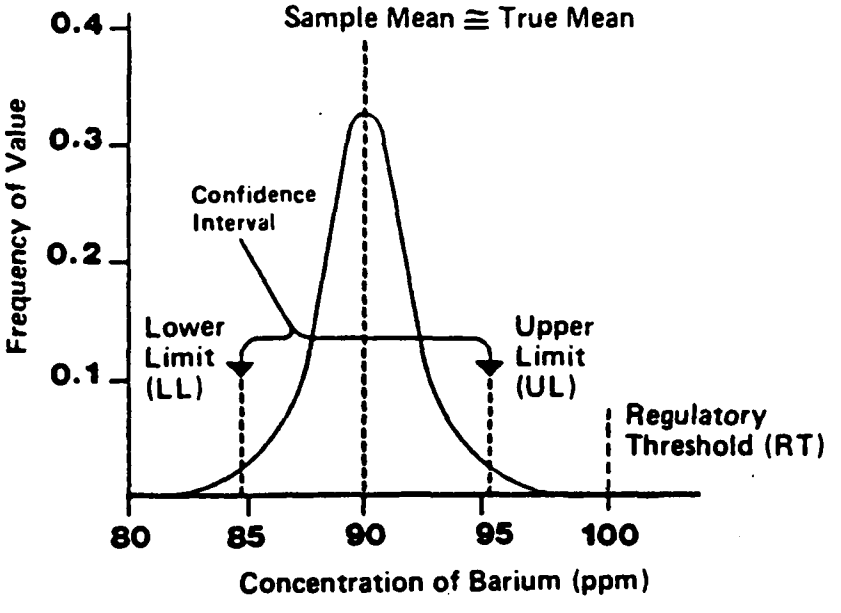
By asking such questions, both the primary objective and specific sampling, analytical, and data objectives can be established.

Two sampling efforts could have identical primary objectives but different specific objectives. For example, consider two situations in which the primary objective is to determine if the concentration of barium is less than the regulatory threshold of 100 ppm. The specific objectives will vary and have a substantial effect on sampling. (This situation is presented graphically in Figures 9-3 and 9-4.) In Figure 9-3, under the assumption that the true distribution of barium concentrations throughout the waste of interest is as shown, limited information has indicated that the average concentration is approximately 50 ppm. In Figure 9-4, assume that historical data indicated an average concentration of 90 ppm and the true distribution of barium concentrations is as shown. Therefore, the specific data objective for the latter case is to generate a data base that can discriminate between 90 and 100 ppm, whereas in the former case the data objective is to discriminate between 50 and 100 ppm. Greater accuracy and precision are required to discriminate between 90 and 100 ppm; this fact will affect the number, size, and degree of compositing of samples collected and analyzed.



Distance of true value from regulatory threshold requires less accuracy and precision.

Figure 9-3. Distribution of barium concentration removed from a regulatory threshold.



Proximity of true value from regulatory threshold requires more accuracy and precision.

Figure 9-4. Distribution of barium concentration near a regulatory threshold.

The form in Figure 9-5 can be used to document primary and specific objectives prior to development of a sampling plan. Once the objectives of a sampling effort are developed, it is important to adhere to them to ensure that the program maintains its direction.

9.2.2 Sampling Plan Considerations

The sampling plan is usually a written document that describes the objectives and details the individual tasks of a sampling effort and how they will be performed. (Under unusual circumstances, time may not allow for the sampling plan to be documented in writing, e.g., sampling during an emergency spill. When operating under these conditions, it is essential that the person directing the sampling effort be aware of the various elements of a sampling plan.) The more detailed the sampling plan, the less the opportunity for oversight or misunderstanding during sampling, analysis, and data treatment.

To ensure that the sampling plan is designed properly, it is wise to have all aspects of the effort represented. Those designing the sampling plan should include the following personnel:

1. An end-user of the data, who will be using the data to attain program objectives and thus would be best prepared to ensure that the data objectives are understood and incorporated into the sampling plan.

2. An experienced member of the field team who will actually collect samples, who can offer hands-on insight into potential problems and solutions, and who, having acquired a comprehensive understanding of the entire sampling effort during the design phase, will be better prepared to implement the sampling plan.

3. An analytical chemist, because the analytical requirements for sampling, preservation, and holding times will be factors around which the sampling plan will be written. A sampling effort cannot succeed if an improperly collected or preserved sample or an inadequate volume of sample is submitted to the laboratory for chemical, physical, or biological testing. The appropriate analytical chemist should be consulted on these matters.

4. An engineer should be involved if a complex manufacturing process is being sampled. Representation of the appropriate engineering discipline will allow for the optimization of sampling locations and safety during sampling and should ensure that all waste-stream variations are accounted for.

5. A statistician, who will review the sampling approach and verify that the resulting data will be suitable for any required statistical calculations or decisions.

6. A quality assurance representative, who will review the applicability of standard operating procedures and determine the number of blanks, duplicates, spike samples, and other steps required to document the accuracy and precision of the resulting data base.

Sampling Site: _____

_____

_____

Address: _____

_____

_____

Description of Waste to be Sampled: _____

_____

_____

Primary Objective: _____

_____

_____

Specific Sampling Objectives: _____

_____

_____

Specific Analysis Objectives: _____

_____

_____

Specific Data Objectives: _____

_____

_____

Figure 9-5. Form for Documenting Primary and Specific Objectives

At least one person should be familiar with the site to be sampled. If not, then a presampling site visit should be arranged to acquire site-specific information. If no one is familiar with the site and a presampling site visit cannot be arranged, then the sampling plan must be written so that it can address contingencies that may occur.

Even in those cases in which a detailed sampling plan is authored and a comprehensive knowledge of the site exists, it is unusual for a sampling plan to be implemented exactly as written. Waste-stream changes, inappropriate weather, sampling equipment failure, and problems in gaining access to the waste are some reasons why a sampling plan must be altered. Thus it is always necessary to have at least one experienced sampler as a member of a sampling team.

The sampling plan should address the considerations discussed below.

9.2.2.1 Statistics

A discussion of waste sampling often leads to a discussion of statistics. The goals of waste sampling and statistics are identical, i.e., to make inferences about a parent population based upon the information contained in a sample.

Thus it is not surprising that waste sampling relies heavily upon the highly developed science of statistics and that a sampling/analytical effort usually contains the same elements as does a statistical experiment. Analogously, the Harris pollster collects opinions from randomly chosen people, whereas environmental scientists collect waste at randomly chosen locations or times. The pollster analyzes the information into a useable data base; laboratories analyze waste samples and generate data. Then the unbiased data base is used to draw inferences about the entire population, which for the Harris pollster may be the voting population of a large city, whereas for the environmental scientist the population may mean the entire contents of a landfill.

During the implementation of a waste sampling plan or a statistical experiment, an effort is made to minimize the possibility of drawing incorrect inferences by obtaining samples that are representative of a population. In fact, the term "representative sample" is commonly used to denote a sample that (1) has the properties and chemical composition of the population from which it was collected, and (2) has them in the same average proportions as are found in the population.

In regard to waste sampling, the term "representative sample" can be misleading unless one is dealing with a homogeneous waste from which one sample can represent the whole population. In most cases, it would be best to consider a "representative data base" generated by the collection and analysis of more than one sample that defines the average properties or composition of the waste. A "representative data base" is a more realistic term because the evaluation of most wastes requires numerous samples to determine the average properties or concentrations of parameters in a waste. (The additional samples needed to generate a representative data base can also be used to determine the variability of these properties or concentrations throughout the waste population.)

Statisticians have developed a number of strategies to obtain samples that are unbiased and collectively representative of a population. A detailed discussion of these strategies is presented in Section 9.1 of this chapter. The following discussion of statistical considerations is a less technical summary of these strategies. It was written to complement Section 9.1 and will be most useful after Section 9.1 is read and studied.

Section 9.1 describes three basic sampling strategies: simple random, stratified random, and systematic random sampling. It should be noted that the word random has more than one meaning. When used in statistical discussions, it does not mean haphazard; it means that every part of a waste has a theoretically equal chance of being sampled. Random sampling, which entails detailed planning and painstaking implementation, is distinctly different from haphazard sampling, which may introduce bias into the collection of samples and the resulting data.

Systematic random sampling and authoritative sampling strategies require a substantial knowledge of the waste to ensure that: (1) a cycle or trend in waste composition does not coincide with the sampling locations; or (2) in the case of authoritative sampling, all or most of the assumptions regarding waste composition or generation are true. Because the variabilities of waste composition and the waste generation process are often unknown, systematic random and authoritative sampling strategies are usually not applicable to waste evaluation.

Therefore, for waste sampling, the usual options are simple or stratified random sampling. Of these two strategies, simple random sampling is the option of choice unless: (1) there are known distinct strata (divisions) in the waste over time or in space; (2) one wants to prove or disprove that there are distinct time and/or space strata in the waste of interest; or (3) one is collecting a minimum number of samples and desires to minimize the size of a hot spot (area of high concentration) that could go unsampled. If any of these three conditions exists, it may be determined that stratified random sampling would be the optimum strategy. To explain how these strategies can be employed, a few examples follow:

Example 1: Simple Random Sampling of Tanks

A batch manufacturing process had been generating a liquid waste over a period of years and storing it in a large open-top tank. As this tank approached capacity, some of the waste was allowed to overflow to a smaller enclosed tank. This smaller tank allowed for limited access through an inspection port on its top.

Because the on-site tank storage was approaching capacity, it was determined that the waste would have to be disposed of off-site.

The operators of the facility had determined that the waste was a nonhazardous solid waste when the RCRA regulations were first promulgated. However, upon recent passage of more stringent state regulations and concerns of potential liability, the operators determined that they should perform a more comprehensive analysis of the waste.

Because the waste was generated in a batch mode over a period of years, the operators were concerned that the waste composition might have varied between batches and that stratification might have occurred in the tank at unknown and random depths. Based on their knowledge, the operators knew that a grab sample would not suffice and that a sampling program would have to be designed to address the heterogeneity of the waste.

Because the operators intended to dispose of the entire contents of the tank and lacked any specific information regarding stratification and variability of the waste, it was decided that a simple random strategy would be employed. (If the operators had treated portions of the waste differently or had been aware of distinct strata, then stratified random sampling might have been more appropriate.)

The large, unenclosed tank had a diameter of 50 ft, a height of 20 ft, and an approximate volume of 295,000 gal allowed. It was encircled and traversed by catwalks (refer to Figure 9-6), which allowed access to the entire waste surface. The smaller tank had a diameter of 10 ft, a height of 10 ft, and an approximate volume of 6,000 gal; an inspection port located on the top allowed limited access. It was determined that the different construction of the two tanks would require different simple random sampling approaches.

In the case of the large tank, it was decided that vertical composite samples would be collected because the operators were interested in the average composition and variability of the waste and not in determining if different vertical strata existed. It was decided to select points randomly along the circumference (157 ft) and along the radius (25 ft). These numbers, which would constitute the coordinates of the sampling locations, were chosen from a random-number table by indiscriminately choosing a page and then a column on that page. The circumference coordinates were then chosen by proceeding down the column and listing the first 15 numbers that are greater than or equal to 0, but less than or equal to 157. The radius coordinates were chosen by continuing down the column and listing the first 15 numbers that are greater than or equal to 0, but less than or equal to 25. These numbers were paired to form the coordinates that determined the location of the 15 randomly chosen sampling points. These coordinates were recorded in the field notebook (refer to Table 9-3). Because no precision data on waste composition existed prior to sampling, the number of samples (15) was chosen as a conservative figure to more than allow for a sound statistical decision.

The actual samples were collected by employing a sampling device, which was constructed on site from available materials, and a weighted bottle. This device, which was used to access more remote areas of the tank, consisted of a weighted bottle, a rope marked off at 1-ft increments, and a discarded spool that originally contained electrical wire (refer to Figure 9-7).

Samples were collected by a three-person team. The person controlling the weighted bottle walked to the first circumference coordinate (149 ft), while the two persons holding the ropes attached to the spool walked along opposing catwalks toward the center of the tank. The person controlling the

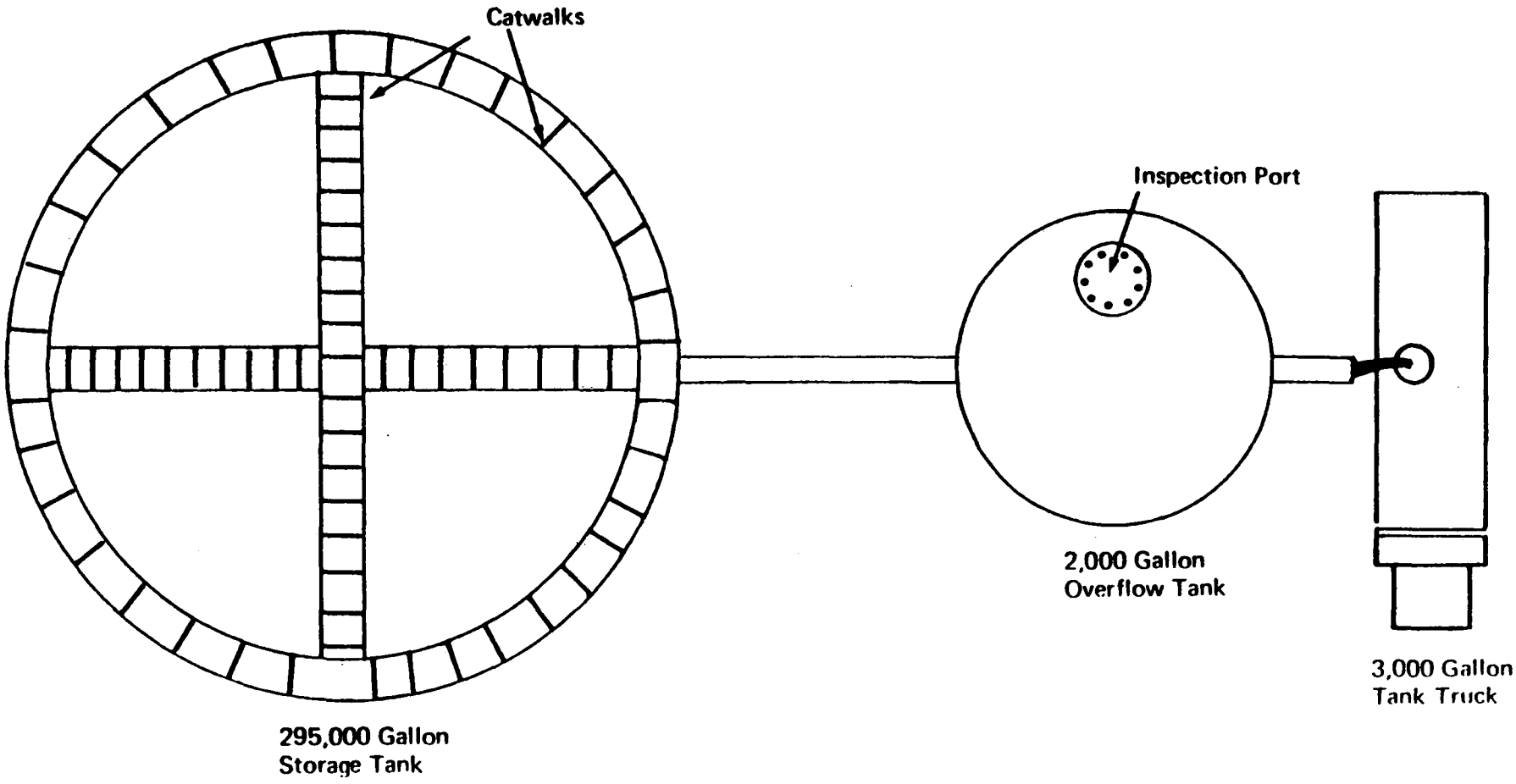


Figure 9-6. Bird's eye view of waste tank, overflow tank, tank truck and connecting plumbing.

TABLE 9-3. RANDOM COORDINATES FOR 295,000-GAL TANK

Sampling point	Circumference	Radius
1	149	4
2	86	22
3	94	13
4	99	0
5	23	10
6	58	2
7	52	22
8	104	16
9	23	25
10	51	4
11	77	14
12	12	5
13	151	15
14	83	23
15	99	18

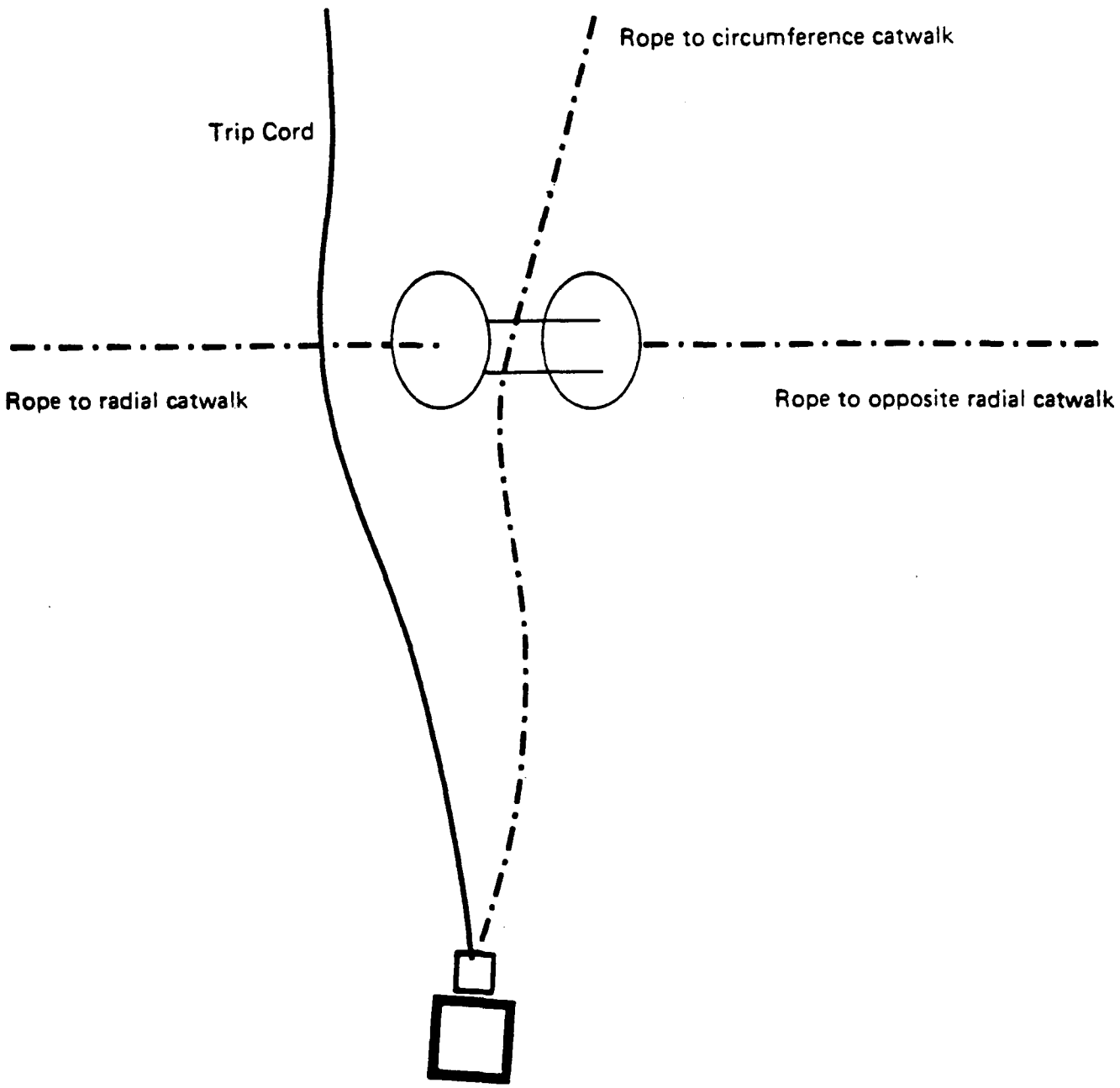


Figure 9-7. Device used to collect sample from the open tank.

weighted bottle measured off the radius coordinate (4 ft). The spool was then centered in the quadrant, the weighted bottle was lowered to the surface, and a sample was collected from the first 2 ft of waste. This sample was then transferred into a large, labeled sample container, which was used for compositing. This same process was repeated nine more times at the same location at different 2-ft depth intervals, resulting in the collection of a total of 10 component depth samples that were compiled in the field into one sample for that sampling point. This process was repeated at the remaining 14 sampling points, resulting in the collection of 15 vertical composite samples. These vertical composite samples were taken to address any vertical stratification that may have occurred.

The samples were properly preserved and stored, chain-of-custody procedures were completed, and the samples were submitted to the laboratory. A cost/benefit decision was made to composite aliquots of the samples into five composite samples that were submitted for analysis. (Following analysis, Equation 8 of Section 9.1 of this chapter was employed to determine if enough samples were analyzed to make a statistically sound decision. If the number of samples analyzed was not sufficient, then the samples would be recomposited to a lesser degree or analyzed individually.)

Because there was no information to prove that the waste in the smaller tank was the same as that in the larger tank, the operators decided that the smaller tank must also be sampled. The different construction of the smaller, enclosed tank mandated that a different sampling plan be designed. The only access to the tank was through a small inspection port on the top of the tank. This port would allow sampling only of a small portion of the tank contents; thus, to make a decision on the entire contents of the tank, one would have to assume that the waste in the vicinity of the inspection port was representative of the remainder of the tank contents. The operators were not willing to make this assumption because they determined that the liability of an incorrect decision overrode the convenience of facilitating the sampling effort.

To randomly sample the entire contents of the tank, a different plan was designed. This plan exploited the relatively small volume (approximately 6,000 gal) of the tank. A decision was made to rent two tank trucks and to sample the waste randomly over time as it drained from the tank into the tank trucks.

It was calculated that at a rate of 20 gal/min, it would take 300 min to drain the tank. From the random-number tables, 15 numbers that were greater than or equal to 0, but less than or equal to 300, were chosen in a manner similar to that employed for the larger tank. These numbers were recorded in the field notebook (refer to Table 9-4) at the time that they were encountered in the random-number table and were then assigned sampling point numbers according to their chronological order.

The 15 samples were collected at the previously chosen random times as the waste exited from a drainage hose into the tank trucks. These samples were collected in separate labeled containers, properly preserved and stored; chain-of-custody procedures were employed for transferral of the samples to the laboratory.

TABLE 9-4. RANDOM TIMES FOR 6,000-GAL TANK

Sampling point	Time (min)
11	153
10	122
8	85
6	55
5	46
15	294
12	195
1	5
13	213
9	99
2	29
4	41
7	74
3	31
14	219

The above example employed simple random sampling to determine the average composition and variance of the waste contained in the two tanks. The contents of the large tank were sampled randomly in space, whereas the contents of the smaller tank were sampled randomly over time.

The following example will involve the use of stratified random sampling, which is used when: (1) distinct strata are known to exist or (2) it is not known whether different strata exist, but an objective of the sampling effort is to discover the existence or nonexistence of strata.

A variation of this second reason for employing stratified random sampling is when cost considerations limit the number of samples that can be collected (e.g., when the budget allows for the collection of only six samples in a 40-acre lagoon). In this situation, where little is known about the composition of the waste, a concern exists that an area of the lagoon may be highly contaminated and yet may not be sampled. The smaller the number of samples, the greater the probability that an area of high contamination (a distinct stratum) could be missed, and the greater the probability that the sampling accuracy will suffer. Under such circumstances, a sampling plan may employ stratified random sampling to minimize the size of a highly contaminated area that could go unsampled.

For example, consider the situation where the budget allows only for the collection of six samples in a 40-acre lagoon. If simple random sampling is employed with such a small number of samples, there is a certain probability that large areas of the lagoon may go unsampled. One approach to minimizing the size of areas that may go unsampled is to divide the lagoon into three strata of equal size and randomly sample each stratum separately. This approach decreases the size of an area that can go unsampled to something less than one-third of the total lagoon area.

The following example details more traditional applications of stratified random sampling.

Example 2: Stratified Random Sampling of Effluents and Lagoons

A pigment manufacturing process has been generating wastes over a number of years. The pigment is generated in large batches that involve a 24-hr cycle. During the first 16 hr of the cycle, an aqueous sludge stream is discharged. This waste contains a high percentage of large-sized black particulate matter. The waste generated during the remaining 8 hr of the manufacturing cycle is an aqueous-based white sludge that consists of much smaller-sized particles than those found in the sludge generated in the first 16 hr of the batch process. This waste has been disposed of over the years into a 40-acre settling lagoon, allowing the particulate matter to settle out of solution while the water phase drains to an NPDES outfall at the opposite end of the lagoon. The smaller white pigment particles released in the last 8 hr of the batch process settle more slowly than the much larger black particles generated in the previous 16 hr. This settling pattern is quite apparent from the distinct colors of the wastes. The sludge in the quadrant closest to the waste influent pipe is black; the next quadrant is a light gray color, resulting from settling of both waste streams. The last two quadrants contain a pure white sludge, resulting from the settling of the small pigment particles.

Eventually, the facility operators decided that the settled particulate matter had to be removed to keep the settling lagoon functioning. In the past, this residual lagoon waste was found to be a hazardous waste due to its leachable barium content. Further studies determined that the source of the barium was a certain raw material that was released during the first 16 hr of batch process.

To minimize present disposal costs, the operators wanted to determine if the white sludge in the last two quadrants and the light gray waste were nonhazardous. Also, the operators had recently changed raw materials, with the intention of removing the source of barium in an attempt to minimize future disposal costs. Thus, the operators were interested in determining whether the currently generated waste was hazardous. If the altered waste stream was not hazardous, future lagoon sludge could be disposed of more economically as a solid waste. If the waste generated during the first 16 hr of the process remained hazardous but the waste generated during the following 8 hr was nonhazardous, the operators were willing to shift this latter waste to a second lagoon reserved for nonhazardous wastes. By sequestering the waste streams in this manner, the operators intended to decrease the amount of hazardous waste by precluding generation of additional amounts of hazardous waste under the "mixture rule."

To decide how the lagoon sludge should be handled, the operators arranged to have the lagoon sludge sampled. The objectives of sampling the lagoon sludge were to determine the average concentration and variance of leachable barium for the sludge in the entire lagoon and for each of the different sludges.

The dimensions of the 40-acre square lagoon were calculated to be 1,320 ft on a side, with the black and the gray sludge each covering a quadrant measuring 1,320 ft by 330 ft, and the white sludge covering the remaining area of the lagoon, which measured 1,320 ft by 660 ft (refer to Figure 9-8). The sludge had settled to a uniform thickness throughout the lagoon and was covered with 2 ft of water.

Because the leachable barium was assumed to be associated with the black sludge, which was concentrated in the first quadrant, a stratified random sampling approach was chosen. (Because of the obvious strata in the lagoon sludge, the stratified sampling strategy was expected to give a more precise estimate of the leachable barium, in addition to giving information specific to each stratum.)

When the actual sampling was being planned, it was decided that the hazards presented by the lagoon waste were minimal, and, that if proper precautions were employed, a stable and unsinkable boat could be used to collect samples. The samples were collected with a core sampler at random locations throughout each stratum. Because the cost of collecting samples was reasonable and no historical data were available to help determine the optimum number of samples, the operators decided to collect a total of 10 samples from each of the smaller strata and a total of 20 samples from the larger strata. They had confidence that this number of samples would allow them to detect a small significant difference between the mean concentration of leachable barium and the applicable regulatory threshold.

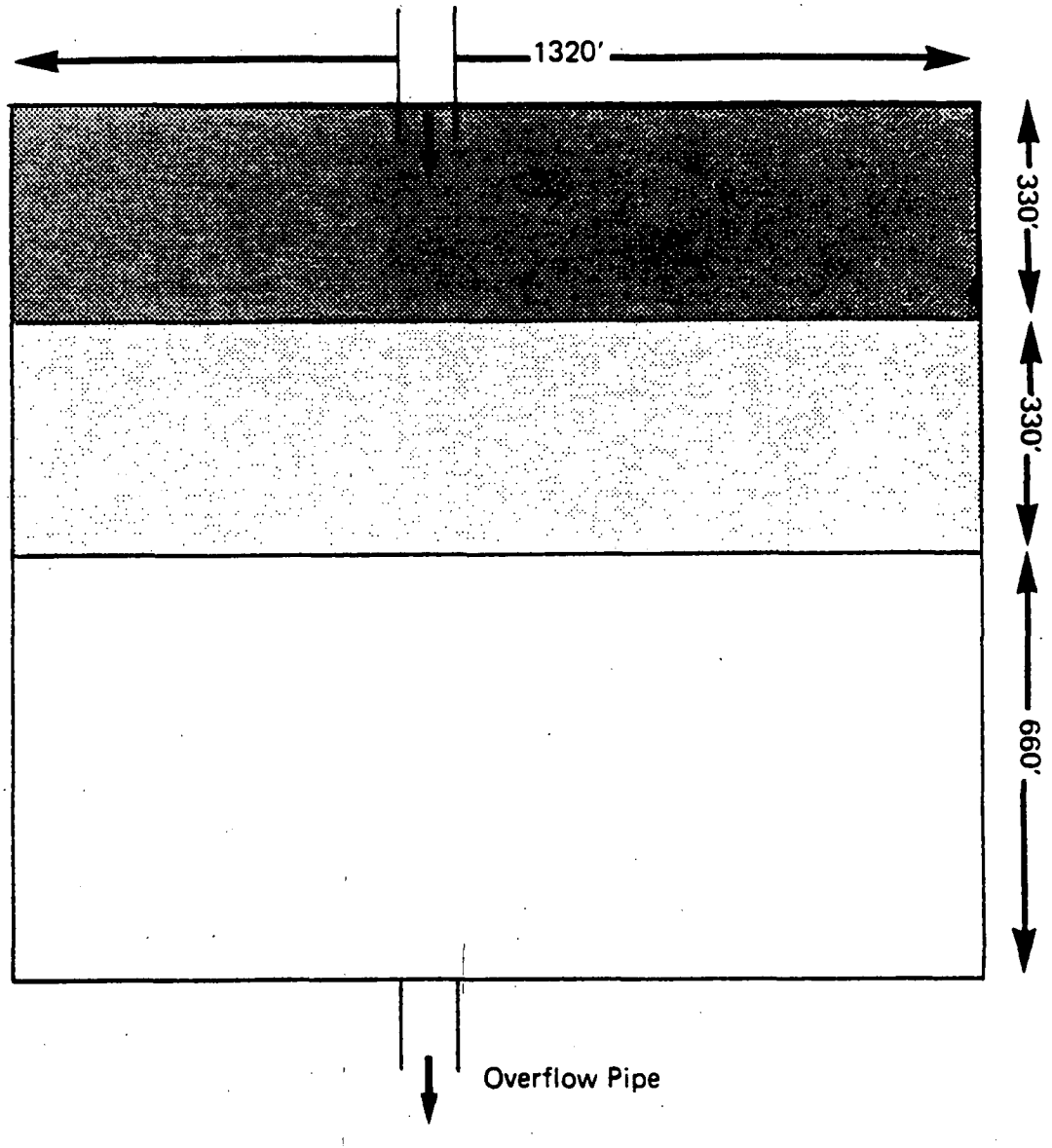


Figure 9-8. Schematic of the 40-acre settling lagoon displaying strata generated by a waste stream.

The locations of the random sampling points were determined by selecting length and width coordinates from a random-number table. This was done by indiscriminately choosing a page from the random-number tables and then a column on that page. The width coordinates of the two smaller quadrants were then chosen by proceeding down the column and listing the first 20 numbers that were greater than or equal to 0, but less than or equal to 330. The width coordinate for the third and largest stratum was chosen by proceeding down the column and selecting the first 20 numbers that were greater than or equal to 0, but less than or equal to 660. Because the lengths of the three quadrants were all 1,320 ft, the length coordinates were chosen by listing the first 40 numbers that were greater than or equal to 0 but less than or equal to 1,320. These coordinates were recorded in the field notebook (refer to nable 9-5).

The samples were collected by a four-person team. Two people remained onshore while two maneuvered the boat and collected the samples. The first sample in the first quadrant was collected by launching the boat at a distance of 41 ft from the corner, which was designated the origin, 0 ft. The boat proceeded out into the lagoon perpendicular to the long side of the quadrant. The person onshore released 134 ft of a measured rope, which allowed the boat to stop at the first sampling point (41, 134). The sample was then collected with a core sampler and transferred to a sample container. This process was repeated for all sampling points in the three strata. The samples were properly preserved and stored, and the chain-of-custody records documented the transfer of samples to the laboratory.

Aliquots of the samples were composited into five composite samples for each stratum. The mean and variance of each stratum were calculated by Equations 2(a) and 3(a), respectively. The mean and variance for the total lagoon were calculated by using Equations 2(b) and 3(b), respectively. Equation 6 was used to calculate a confidence interval for the leachable barium concentration, and the upper limit of this interval was compared with the regulatory threshold. (See Table 9-1, Section 9.1 of this chapter, for equations.)

As previously mentioned, the operators had recently changed their raw materials and were also interested in discovering if the currently generated waste was nonhazardous or if portions of this waste stream were nonhazardous. As described above, the waste effluent for the first 16 hr of the day was different from that discharged during the last 8 hr. However, because the same large plumbing system was used for both waste streams, there were two 2-hr periods during which the discharged waste was a mixture of the two different wastes.

With the above objectives in mind, the operators decided to employ stratified random sampling with four strata occurring over time, as opposed to the strata in space that were employed for sampling the lagoon. The four time strata were from 6:00 to 8:00 hr, from 8:00 to 20:00 hr, from 20:00 to 22:00 hr, and from 22:00 to 6:00 hr the following day. The two 2-hr strata were those time periods during which the waste was a mixture of the two different waste streams. The 12-hr stratum was the time period during which the large-sized particulate black waste was being discharged. The smaller particulate white waste was being discharged during the 8-hr stratum.

TABLE 9-5. RANDOM COORDINATES FOR EACH STRATUM IN THE 40-ACRE SETTLING LAGOON

	Sampling Point	Length (ft)	Width (ft)
Stratum #1 (Black)	1	41	134
	2	271	51
	3	968	32
	4	129	228
	5	472	137
	6	1,198	56
	7	700	261
	8	286	8
	9	940	26
	10	151	121
Stratum #2 (Gray)	1	1,173	109
	2	277	2
	3	438	302
	4	780	5
	5	525	135
	6	50	37
	7	26	127
	8	1,207	149
	9	1,231	325
	10	840	32
Stratum #3 (White)	1	54	374
	2	909	434
	3	1,163	390
	4	1,251	449
	5	1	609
	6	1,126	140
	7	717	235
	8	1,155	148
	9	668	433
	10	66	642
	11	462	455
	12	213	305
	13	1,220	541
	14	1,038	644
	15	508	376
	16	1,293	270
	17	30	38
	18	114	52
	19	1,229	570
	20	392	613

The flow rate was constant throughout the 24-hr period, and there were no precision data available for the waste. Therefore, it was decided that the number of samples collected in the 8- and 12-hr strata would be proportional to time. Because the 2-hr periods were times during which the composition of the waste was changing, it was decided to collect more samples to get a more precise estimate of the average composition of the waste during these time strata. Thus a total of 28 samples was collected.

The samples were collected at randomly chosen times within each time stratum. The random sampling times were chosen by employing a random-number table. After indiscriminately selecting a starting point, the first four numbers greater than or equal to 0, but less than or equal to 120 were selected for the 120-min strata from 6:00 to 8:00 hr. These minutes were then added to the starting time to determine when the four samples would be collected. In similar fashion, the remaining 24 sampling times were chosen. The random-number data were recorded in a laboratory notebook (refer to Table 9-6).

The samples were collected from the waste influent pipe with a wide-mouth bottle at the randomly chosen sampling times. The samples were properly preserved and stored and shipped to the laboratory, along with chain-of-custody records. The samples were subjected to analysis, and the data were evaluated in a manner similar to that employed for the samples of sludge collected in the different strata of the lagoon.

9.2.2.2 Waste

The sampling plan must address a number of factors in addition to statistical considerations. Obviously, one of the most important factors is the waste itself and its properties. The following waste properties are examples of what must be considered when designing a sampling plan:

1. Physical state: The physical state of the waste will affect most aspects of a sampling effort. The sampling device will vary according to whether the sample is liquid, gas, solid, or multiphasic. It will also vary according to whether the liquid is viscous or free-flowing, or whether the solid is hard or soft, powdery, monolithic, or clay-like.

   Wide-mouth sample containers will be needed for most solid samples and for sludges or liquids with substantial amounts of suspended matter. Narrow-mouth containers can be used for other wastes, and bottles with air-tight closures will be needed for gas samples or gases adsorbed on solids or dissolved in liquids.

   The physical state will also affect how sampling devices are deployed. A different plan will be developed for sampling a soil-like waste that can easily support the weight of a sampling team and its equipment than for a lagoon filled with a viscous sludge or a liquid waste.

TABLE 9-6. RANDOM TIMES FOR THE WASTE EFFLUENT

	Sampling Point	Random Minute	Time
Stratum #1 (6:00 to 8:00 hours)	1	28	6:28
	2	62	7:02
	3	99	7:39
	4	112	7:52
Stratum #2 (8:00 to 20:00 hours)	1	11	8:11
	2	107	9:47
	3	156	10:36
	4	173	10:53
	5	296	12:56
	6	313	13:13
	7	398	14:38
	8	497	16:17
	9	555	17:15
	10	600	18:00
	11	637	18:37
	12	706	19:46
Stratum #3 (20:00 to 22:00 hours)	1	13	20:13
	2	52	20:52
	3	88	21:28
	4	108	21:48
Stratum #4 (22:00 to 6:00 hours	1	48	22:48
	2	113	23:53
	3	153	24:33
	4	189	1:09
	5	227	1:47
	6	290	2:49
	7	314	3:14
	8	474	5:44

The sampling strategy will have to vary if the physical state of the waste allows for stratification (e.g., liquid wastes that vary in density or viscosity or have a suspended solid phase), homogenization or random heterogeneity.

2. Volume: The volume of the waste, which has to be represented by the samples collected, will have an effect upon the choice of sampling equipment and strategies. Sampling a 40-acre lagoon requires a different approach from sampling a 4-sq-ft container. Although a 3-ft depth can be sampled with a Coliwasa or a drum thief, a weighted bottle may be required to sample a 50-ft depth.

3. Hazardous properties: Safety and health precautions and methods of sampling and shipping will vary dramatically with the toxicity, ignitability, corrosivity, and reactivity of the waste.

4. Composition: The chosen sampling strategy will reflect the homogeneity, random heterogeneity, or stratification of the waste in time or over space.

9.2.2.3 Site

Site-specific factors must be considered when designing a sampling plan. A thorough examination of these factors will minimize oversights that can affect the success of sampling and prevent attainment of the program objectives. At least one person involved in the design and implementation of the sampling plan should be familiar with the site, or a presampling site visit should be arranged. If nobody is familiar with the site and a visit cannot be arranged, the sampling plan must be written to account for the possible contingencies. Examples of site-specific factors that should be considered follow:

1. Accessibility: The accessibility of waste can vary substantially. Some wastes are accessed by the simple turning of a valve; others may require that an entire tank be emptied or that heavy equipment be employed. The accessibility of a waste at the chosen sampling location must be determined prior to design of a sampling plan.

2. Waste generation and handling: The waste generation and handling process must be understood to ensure that collected samples are representative of the waste. Factors which must be known and accounted for in the sampling plan include: if the waste is generated in batches; if there is a change in the raw materials used in a manufacturing process; if waste composition can vary substantially as a function of process temperatures or pressures; and if storage time after generation may vary.

3. Transitory events: Start-up, shut-down, slow-down, and maintenance transients can result in the generation of a waste that is not representative of the normal waste stream. If a sample was unknowingly collected at one of these intervals, incorrect conclusions could be drawn.

4. Climate: The sampling plan should specify any clothing needed for personnel to accommodate any extreme heat or cold that may be encountered. Dehydration and extensive exposure to sun, insects, or poisonous snakes must be considered.

5. Hazards: Each site can have hazards -- both expected and unexpected. For example, a general understanding of a process may lead a sampling team to be prepared for dealing with toxic or reactive material, but not for dealing with an electrical hazard or the potential for suffocation in a confined space. A thorough sampling plan will include a health and safety plan that will counsel team members to be alert to potential hazards.

9.2.2.4 Equipment

The choice of sampling equipment and sample containers will depend upon the previously described waste and site considerations. For the following reasons, the analytical chemist will play an important role in the selection of sampling equipment:

1. The analytical chemist is aware of the potential interactions between sampling equipment or container material with analytes of interest. As a result, he/she can suggest a material that minimizes losses by adsorption, volatilization, or contamination caused by leaching from containers or sampling devices.

2. The analytical chemist can specify cleaning procedures for sampling devices and containers that minimize sample contamination and cross contamination between consecutive samples.

3. The analytical chemist's awareness of analyte-specific properties is useful in selecting the optimum equipment (e.g., choice of sampling devices that minimize agitation for those samples that will be subjected to analysis for volatile compounds).

The final choice of containers and sampling devices will be made jointly by the analytical chemist and the group designing the sampling plan. The factors that will be considered when choosing a sampling device are:

1. Negative contamination: The potential for the measured analyte concentration to be artificially low because of losses from volatilization or adsorption.

2. Positive contamination: The potential for the measured analyte to be artifically high because of leaching or the introduction of foreign matter into the sample by particle fallout or gaseous air contaminants.

3. Cross contamination: A type of positive contamination caused by the introduction of part of one sample into a second sample during sampling, shipping, or storage.

4. Required sample volume for physical and/or chemical analysis.

5. "Ease of use" of the sampling device and containers under the conditions that will be encountered on-site. This includes the ease of shipping to and from the site, ease of deployment, and ease of cleaning.

6. The degree of hazard associated with the deployment of one sampling device versus another.

7. Cost of the sampling device and of the labor for its deployment.

This section describes examples of sampling equipment and suggests potential uses for this equipment. Some of these devices are commercially available, but others will have to be fabricated by the user. The information in this section is general in nature and therefore limited.

Because each sampling situation is unique, the cited equipment and applications may have to be modified to ensure that a representative sample is collected and its physical and chemical integrity are maintained. It is the responsibility of those persons conducting sampling programs to make the appropriate modifications.

Table 9-7 contains examples of sampling equipment and potential applications. It should be noted that these suggested sampling devices may not be applicable to a user's situation due to waste- or site-specific factors. For example, if a waste is highly viscous or if a solid is clay-like, these properties may preclude the use of certain sampling devices. The size and depth of a lagoon or tank, or difficulties associated with accessing the waste, may also preclude use of a given device or require modification of its deployment.

The most important factors to consider when choosing containers for hazardous waste samples are compatibility with the waste, cost, resistance to breakage, and volume. Containers must not distort, rupture, or leak as a result of chemical reactions with consitituents of waste samples. Thus, it is important to have some idea of the properties and composition of the waste. The containers must have adequate wall thickness to withstand handling during sample collection and transport to the laboratory. Containers with wide mouths are often desirable to facilitate transfer of samples from samplers to containers. Also, the containers must be large enough to contain the optimum sample volume.

Containers for collecting and storing hazardous waste samples are usually made of plastic or glass. Plastics that are commonly used to make the containers include high-density or linear polyethylene (LPE), conventional polyethylene, polypropylene, polycarbonate, Teflon FEP (fluorinated ethylene propylene), polyvinyl chloride (PVC), or polymethylpentene. Teflon FEP is almost universally usable due to its chemical inertness and resistance to breakage. However, its high cost severely limits its use. LPE, on the other hand, usually offers the best combination of chemical resistance and low cost when samples are to be analyzed for inorganic parameters.

TABLE 9-7. EXAMPLES OF SAMPLING EQUIPMENT FOR PARTICULAR WASTE TYPES

	Waste location or container								
Waste type	Drum	Sacks and bags	Open-bed truck	Closed-bed truck	Storage tanks or bins	Waste piles	Ponds, lagoons, & pits	Conveyor belt	Pipe
Free-flowing liquids and slurries	Coliwasa	N/A	N/A	Coliwasa	Weighted bottle	N/A	Dipper	N/A	Dipper
Sludges	Trier	N/A	Trier	Trier	Trier	a	a		
Moist powders or granules	Trier	Trier	Trier	Trier	Trier	Trier	Trier	Shovel	Dipper
Dry powders or granules	Thief	Thief	Thief	Thief	a	Thief	Thief	Shovel	Dipper
Sand or packed powders and granules	Auger	Auger	Auger	Auger	Thief	Thief	a	Dipper	Dipper
Large-grained solids	Large Trier	Large Trier	Large Trier	Large Trier	Large Trier	Large Trier	Large Trier	Trier	Dipper

[a]This type of sampling situation can present significant logistical sampling problems, and sampling equipment must be specifically selected or designed based on site and waste conditions. No general statement about appropriate sampling equipment can be made.

Glass containers are relatively inert to most chemicals and can be used to collect and store almost all hazardous waste samples, exept those that contain strong alkali and hydrofluoric acid. Glass soda bottles are suggested due to their low cost and ready availability. Borosilicate glass containers, such as Pyrex and Corex, are more inert and more resistant to breakage than soda glass, but are expensive and not always readily available. Glass containers are generally more fragile and much heavier than plastic containers. Glass or FEP containers must be used for waste samples that will be analyzed for organic compounds.

The containers must have tight, screw-type lids. Plastic bottles are usually provided with screw caps made of the same material as the bottles. Buttress threads are recommended. Cap liners are not usually required for plastic containers. Teflon cap liners should be used with glass containers supplied with rigid plastic screw caps. (These caps are usually provided with waxed paper liners.) Teflon liners may be purchased from plastic specialty supply houses (e.g., Scientific Specialties Service, Inc., P.O. Box 352, Randallstown, Maryland 21133). Other liners that may be suitable are polyethylene, polypropylene, and neoprene plastics.

If the samples are to be submitted for analysis of volatile compounds, the samples must be sealed in air-tight containers.

Prior to sampling, a detailed equipment list should be compiled. This equipment list should be comprehensive and leave nothing to memory. The categories of materials that should be considered are:

1. Personnel equipment, which will include boots, rain gear, disposable coveralls, face masks and cartridges, gloves, etc.

2. Safety equipment, such as portable eyewash stations and a first-aid kit.

3. Field test equipment, such as pH meters and Draeger tube samplers.

4. An ample supply of containers to address the fact that once in the field, the sampling team may want to collect 50% more samples than originally planned or to collect a liquid sample, although the sampling plan had specified solids only.

5. Additional sampling equipment for use if a problem arises, e.g., a tool kit.

6. Shipping and office supplies, such as tape, labels, shipping forms, chain-of-custody forms and seals, field notebooks, random-number tables, scissors, pens, etc.

Composite Liquid Waste Sampler (Coliwasa)

The Coliwasa is a device employed to sample free-flowing liquids and slurries contained in drums, shallow tanks, pits, and similar containers. It is especially useful for sampling wastes that consist of several immiscible liquid phases.

The Coliwasa consists of a glass, plastic, or metal tube equipped with an end closure that can be opened and closed while the tube is submerged in the material to be sampled (refer to Figure 9-9).

Weighted Bottle

This sampler consists of a glass or plastic bottle, sinker, stopper, and a line that is used to lower, raise, and open the bottle. The weighted bottle samples liquids and free-flowing slurries. A weighted bottle with line is built to the specifications in ASTM Methods D270 and E300. Figure 9-10 shows the configuration of a weighted-bottle sampler.

Dipper

The dipper consists of a glass or plastic beaker clamped to the end of a two- or three-piece telescoping aluminum or fiberglass pole that serves as the handle. A dipper samples liquids and free-flowing slurries. Dippers are not available commercially and must be fabricated (Figure 9-11).

Thief

A thief consists of two slotted concentric tubes, usually made of stainless steel or brass. The outer tube has a conical pointed tip that permits the sampler to penetrate the material being sampled. The inner tube is rotated to open and close the sampler. A thief is used to sample dry granules or powdered wastes whose particle diameter is less than one-third the width of the slots. A thief (Figure 9-12) is available at laboratory supply stores.

Trier

A trier consists of a tube cut in half lengthwise with a sharpened tip that allows the sampler to cut into sticky solids and to loosen soil. A trier samples moist or sticky solids with a particle diameter less than one-half the diameter of the trier. Triers 61 to 100 cm long and 1.27 to 2.54 cm in diameter are available at laboratory supply stores. A large trier can be fabricated (see Figure 9-13).

Auger

An auger consists of sharpened spiral blades attached to a hard metal central shaft. An auger samples hard or packed solid wastes or soil. Augers are available at hardware and laboratory supply stores.

Scoops and Shovels

Scoops and shovels are used to sample granular or powdered material in bins, shallow containers, and conveyor belts. Scoops are available at laboratory supply houses. Flat-nosed shovels are available at hardware stores.

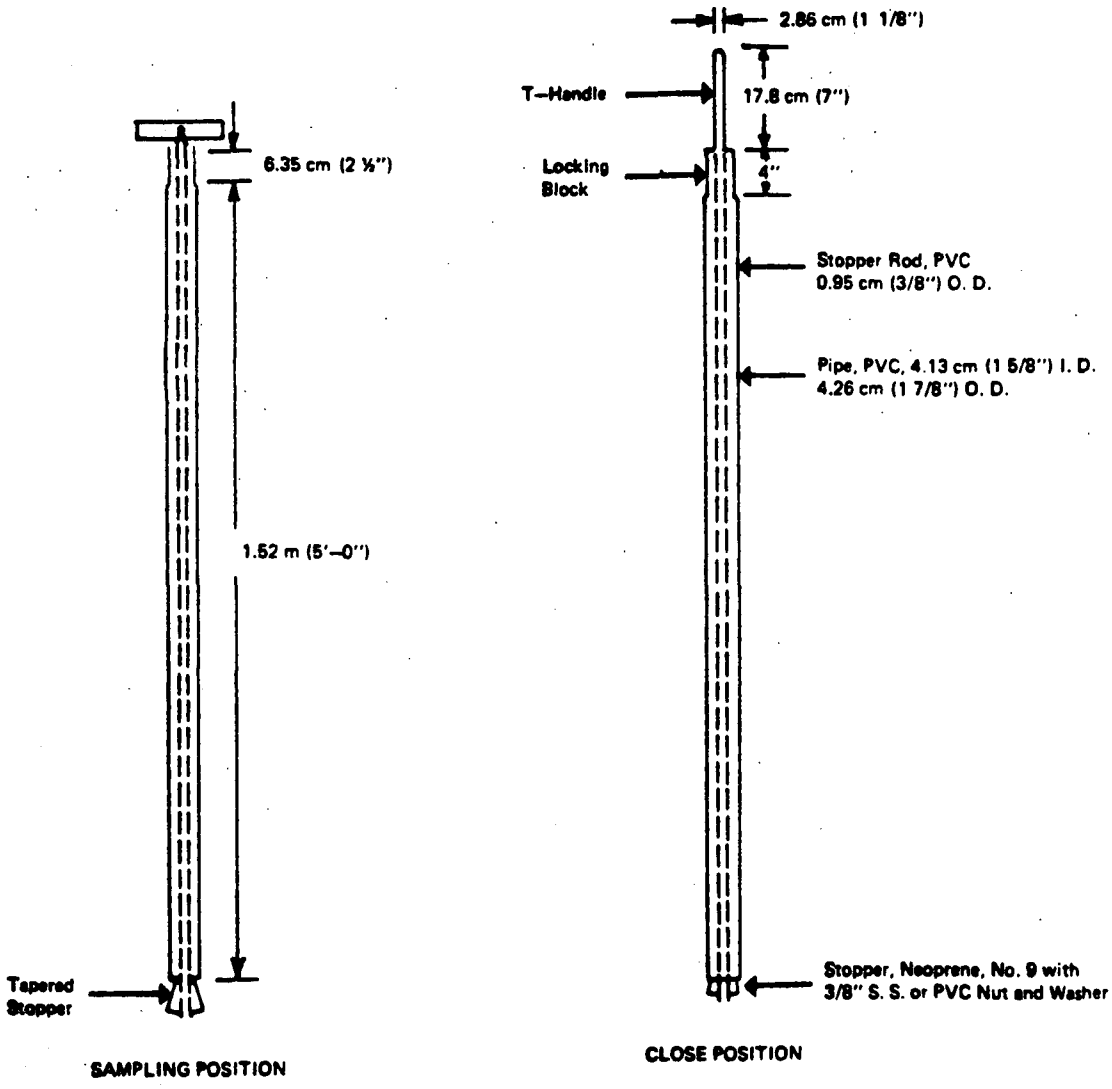


Figure 9-9. Composite liquid waste sampler (Coliwasa).

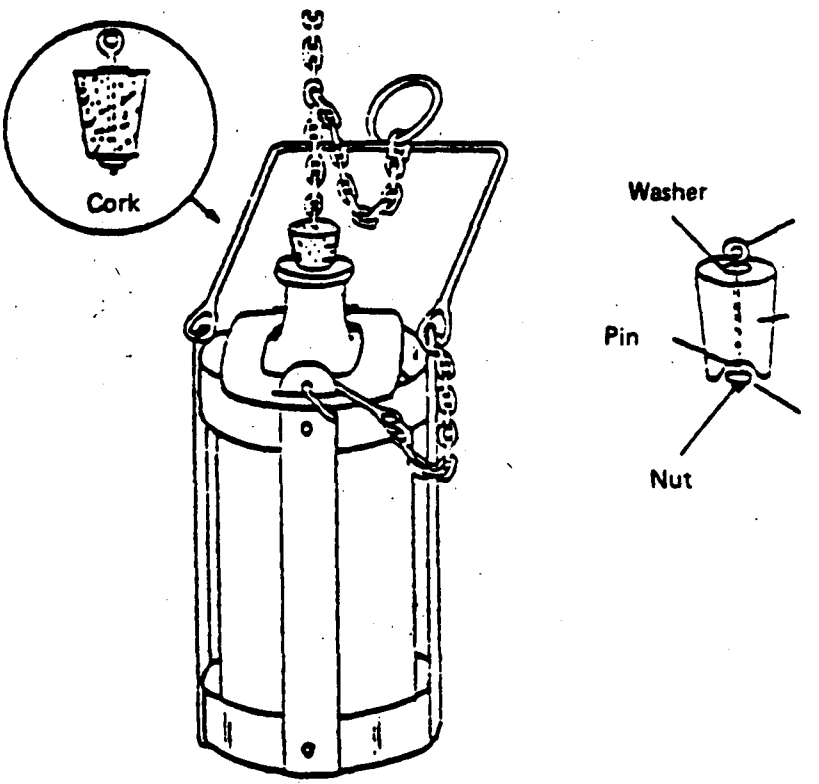


Figure 9-10. Weighted bottle sampler.

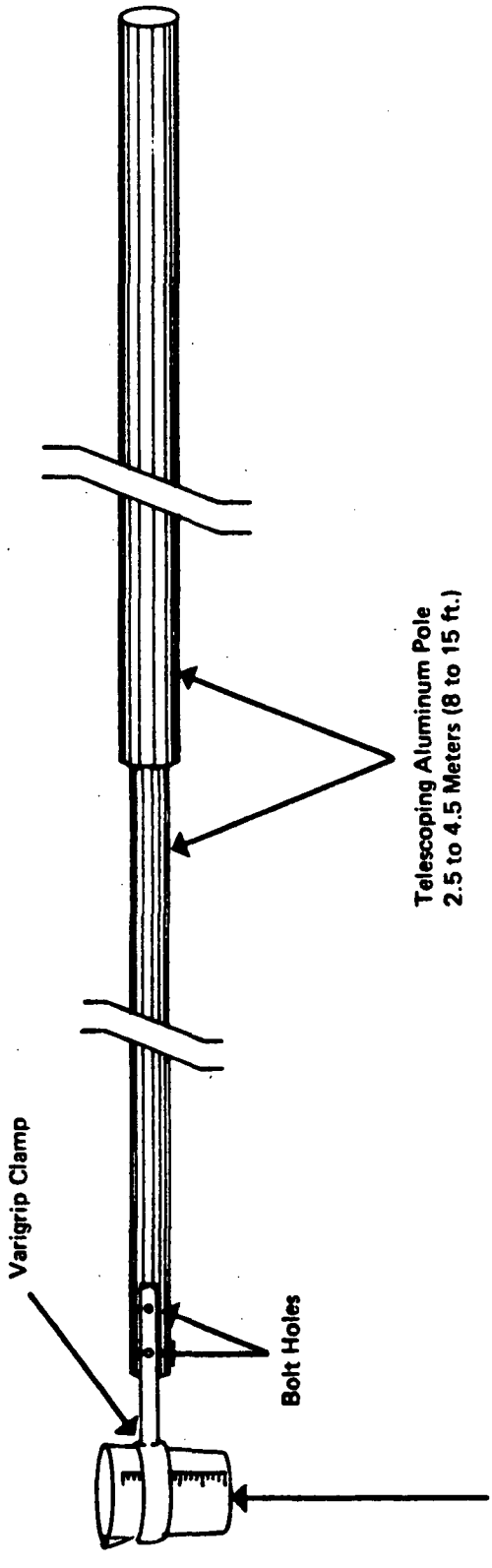


Figure 9-11. Dipper.

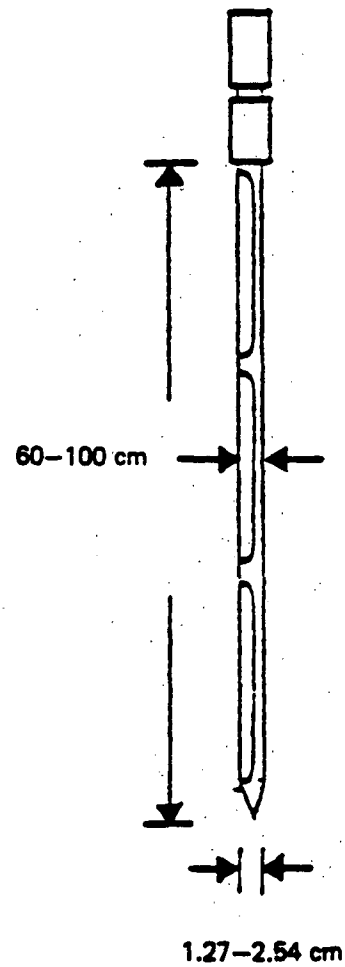
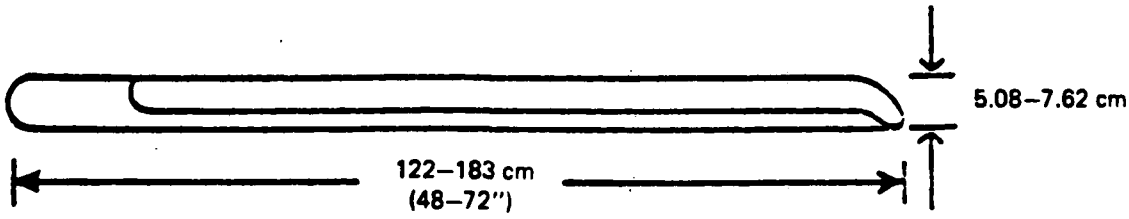


Figure 9-12. Thief sampler.



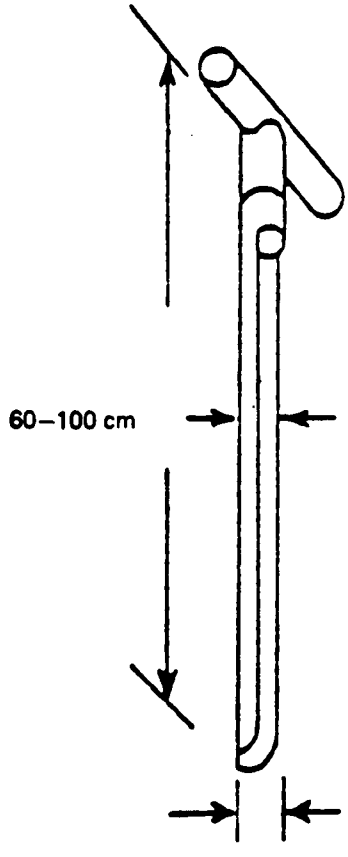


Figure 9-13. Sampling triers.

Bailer

The bailer is employed for sampling well water. It consists of a container attached to a cable that is lowered into the well to retrieve a sample. Bailers can be of various designs. The simplest is a weighted bottle or basally capped length of pipe that fills from the top as it is lowered into the well. Some bailers have a check valve, located at the base, which allows water to enter from the bottom as it is lowered into the well. When the bailer is lifted, the check valve closes, allowing water in the bailer to be brought to the surface. More sophisticated bailers are available that remain open at both ends while being lowered, but can be sealed at both top and bottom by activating a triggering mechanism from the surface. This allows more reliable sampling at discrete depths within a well. Perhaps the best-known bailer of this latter design is the Kemmerer sampler.

Bailers generally provide an excellent means for collecting samples from monitoring wells. They can be constructed from a wide variety of materials compatible with the parameter of interest. Because they are relatively inexpensive, bailers can be easily dedicated to an individual well to minimize cross contamination during sampling. If not dedicated to a well, they can be easily cleaned to prevent cross contamination. Unfortunately, bailers are frequently not suited for well evacuation because of their small volume.

Suction Pumps

As the name implies, suction pumps operate by creating a partial vacuum in a sampling tube. This vacuum allows the pressure exerted by the atmosphere on the water in the well to force water up the tube to the surface. Accordingly, these pumps are located at the surface and require only that a transmission tube be lowered into the well. Unfortunately, their use is limited by their reliance on suction to depths of 20 to 25 ft, depending on the pump. In addition, their use may result in out-gassing of dissolved gases or volatile organics and is therefore limited in many sampling applications. In spite of this, suction methods may provide a suitable means for well evacuation because the water remaining in the well is left reasonably undisturbed.

A variety of pumps that operate on this principle are available, but the ones most commonly suggested for monitoring purposes are the centrifugal and peristaltic pumps. In the centrifugal pump, the fluid is displaced by the action of an impeller rotating inside the pump chamber. This discharges water by centrifugal force. The resulting pressure drop in the chamber creates a suction and causes water to enter the intake pipe in the well. These pumps can provide substantial yields and are readily available and inexpensive. The disadvantages are that they require an external power source and may be difficult to clean between sampling events. In addition, the materials with which these pumps are constructed may frequently be incompatible with certain sample constituents. However, their substantial pumping rates make them suitable for well evacuation.

Peristaltic pumps operate in a manner similar to centrifugal pumps but displace the fluid by mechanical peristalsis. A flexible transmission line is mounted around the perimeter of the pump chamber, and rotating rollers compress the tubing, forcing fluid movement ahead (the peristaltic effect) and inducing suction behind each roller. This design isolates the sample from the moving part of the pump and allows for easy cleaning by removal and replacement of the flexible tubing. Unfortunately, peristaltic pumps are generally capable of providing only relatively low yields. They are, therefore, not ideally suited to well evacuation.

Positive Displacement Pumps

A variety of positive displacement pumps are available for use in withdrawing water from wells. These methods utilize some pumping mechanism, placed in the well, that forces water from the bottom of the well to the surface by some means of positive displacement. This minimizes the potential for aerating or stripping volatile organics from the sample during removal from the well.

The submersible centrifugal pump is one common example of a positive displacement pump. It works in a manner similar to the centrifugal suction lift pump previously described, except that, in this case, both the pump and electric motor are lowered into the well. As the impeller rotates and fluid is brought into the pump, fluid is displaced up the transmission line and out of the well. These pumps are capable of providing a high yield. However, they require an external source of power and are frequently constructed with materials and contain lubricants incompatible with certain sample constituents, particularly organics. They also require considerable equipment and effort to move from well to well. Cleaning between sampling events is difficult as well, and, until recently, they have not been available for well diameters smaller than 3 in.

Piston-driven or reciprocating piston pumps are another example of common positive displacement pumps. These pumps consist of a piston in a submerged cylinder operated by a rod connected to the drive mechanism at the surface. A flap valve or ball-check valve is located immediately above or below the piston cylinder. As the piston is lowered in the cylinder, the check valve opens, and water fills the chamber. On the upstroke, the check valve closes, and water is forced out of the cylinder, up into the transmission line, and to the surface. The transmission line or piston contains a second check valve that closes on the downstroke, preventing water from re-entering the cylinder. These pumps are capable of providing high yields. However, moving these pumps from well to well is difficult, and their use in monitoring programs may require that a pump be dedicated to each well. Many of these pumps may not be constructed with materials compatible with monitoring certain constituents.

A special adaptation of this pump has recently become available for use in ground water monitoring. These piston pumps use compressed gas, rather than a rod connected to a driving mechanism at the surface, to drive the pistons. This provides a much more convenient and portable means for collecting samples from monitoring wells. Compressed-gas pumps provide good yields and can be constructed with materials compatible with many sampling programs.

Another positive displacement pump applicable for monitoring purposes is the gas-operated squeeze pump. This pump was originally developed by R. F. Middleburg of the U.S.G.S. and consequently is referred to as the Middleburg pump. It consists principally of a collapsible membrane inside a long, rigid housing, a compressed gas supply, and appropriate control valves. When the pump is submerged, water enters the collapsible membrane through the bottom check valve. After the membrane has filled, gas pressure is applied to the annular space between the rigid housing and membrane, forcing the water upward through a sampling tube. When the pressure is released, the top check valve prevents the sample from flowing back down the discharge line, and water from the well again enters the pump through the bottom check valve.

Gas-operated squeeze pumps offer a number of advantages for use in ground water monitoring programs. They can be constructed in diameters as small as 1 in. and from a wide variety of materials. They are also relatively portable and are capable of providing a fair range of pumping rates. Most important, the driving gas does not contact the water sample, so that possible contamination or gas stripping does not occur. However, they do require a gas source, and withdrawal of water from substantial depths may require large gas volumes and long pumping cycles.

Jet pumps, a common type of submersible pump used in small domestic water wells, may in some cases be suggested for use in monitoring wells. These pumps operate by injecting water through a pipe down into the well. A venturi device is located at the intake portion of the pump. As the water injected from the surface passes through the constricted portion of the venturi, the velocity increases and pressures decrease according to Bernoulli's principle. If the discharge velocity at the nozzle is great enough, the pressure at this point will be lowered sufficiently to draw water into the venturi assembly through the intake and to bring it to the surface with the original water injected into the well. This additional increment of water is then made available at the surface as the pump's output. Because jet pumps require priming with water and because the water taken from the well mixes with water circulating in the system, they are clearly not applicable to collecting samples for monitoring purposes. For similar reasons, their use is not recommended for well evacuation.

Pressure-Vacuum Lysimeters

The basic construction of pressure-vacuum lysimeters (Wood, 1973), shown in Figure 9-14, consists of a porous ceramic cup, with a bubbling pressure of 1 bar or greater, attached to a short piece of PVC pipe of suitable diameter. Two tubes extend down into the device, as illustrated. Data by Silkworth and Grigal (1981) indicate that, of the two commercially available sampler sizes (2.2 and 4.8 cm diameter), the larger ceramic cup sampler is more reliable, influences water quality less, and yields samples of suitable volume for analysis.

Detailed installation instructions for pressure-vacuum lysimeters are given by Parizek and Lane (1970). Significant modification may be necessary to adapt these instruments to field use when heavy equipment is used. To prevent channelling of contaminated surface water directly to the sampling device, the sampler may be installed in the side wall of an access trench. Because random placement procedures may locate a sampler in the middle of an

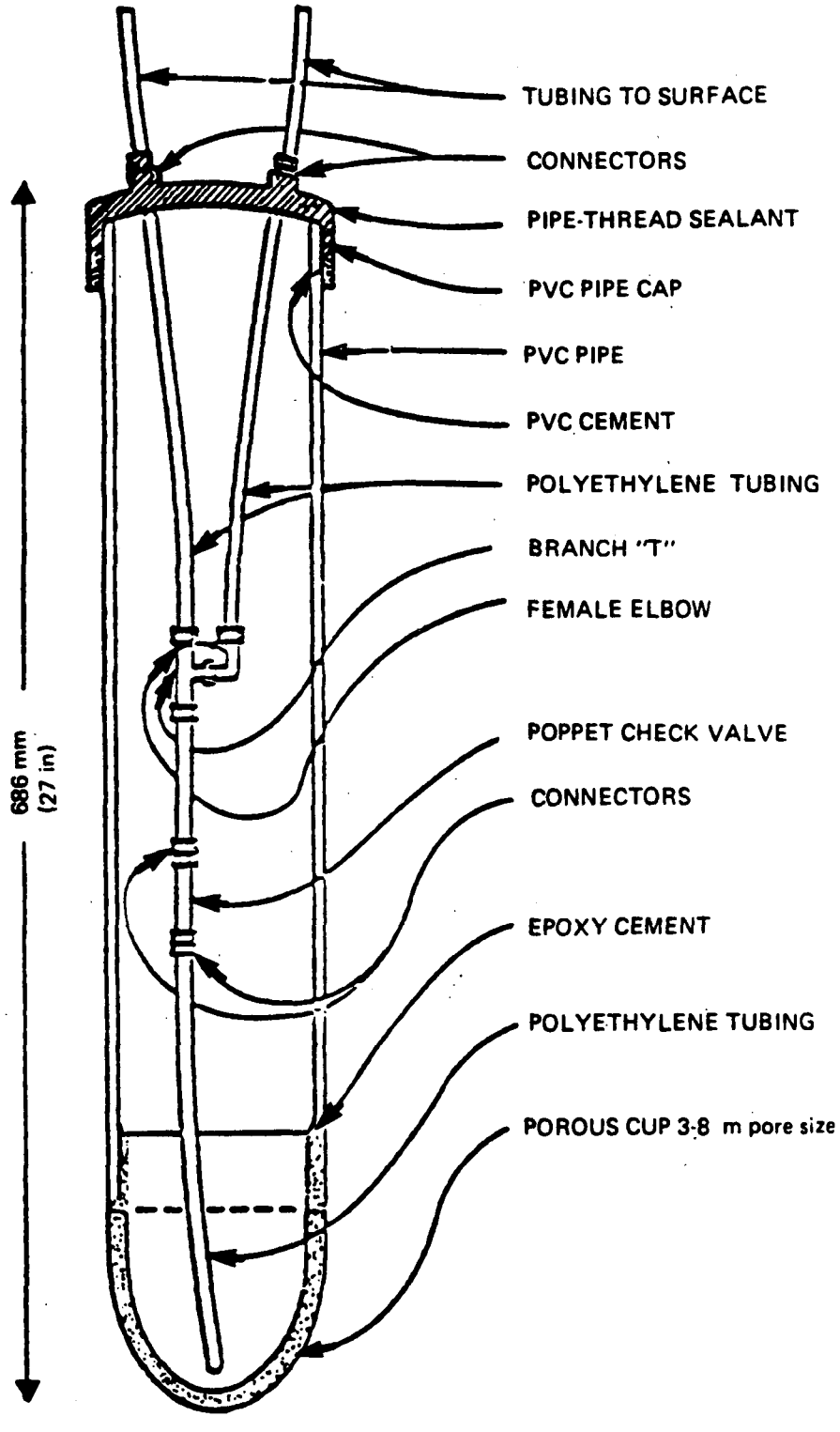


Figure 9-14. One example of a pressure-vacuum lysimeter (Wood, 1973). Reprinted by permission of the American Geophysical Union.

active area, the sample collection tube should be protected at the surface from heavy equipment by a manhole cover, brightly painted steel cage, or other structure. Another problem associated with such sampler placement is that its presence may alter waste management activities (i.e., waste applications, tilling, etc., will avoid the location); therefore, the sampler may not yield representative leachate samples. This problem may be avoided by running the collection tube horizontally underground about 10 m before surfacing.

For sampling after the unit is in place, a vacuum is placed on the system and the tubes are clamped off. Surrounding soil water is drawn into the ceramic cup and up the polyethylene tube. To collect the water sample, the vacuum is released, and one tube is placed in a sample container. Air pressure is applied to the other tube, forcing the liquid up the tube and into the sample container. Preliminary testing should ensure that waste products can pass into the ceramic cup. If sampling for organics, an inert tubing, such as one made of Teflon, should be substituted for the polyethylene pipe to prevent organic contamination.

The major advantages of these sampling devices are that they are easily available, relatively inexpensive to purchase and install, and quite reliable. The major disadvantage is the potential for water quality alterations due to the ceramic cup; this possible problem requires further testing. For a given installation, the device chosen should be specifically tested using solutions containing the soluble hazardous constituents of the waste to be land treated. This device is not recommended for volatiles unless a special trap device is used (Hazardous Waste Land Treatment, SW-874).

Vacuum Extractor

Vacuum extractors were developed by Duke and Haise (1973) to extract moisture from soils above the ground water table. The basic device consists of a stainless steel trough that contains ceramic tubes packed in soil. The unit is sized not to interfere with ambient soil water potentials (Corey, 1974); it is installed at a given depth in the soil with a slight slope toward the collection bottle, which is in the bottom of an adjacent access hole. The system is evacuated and moisture is moved from the adjacent soil into the ceramic tubes and into the collection bottle, from which it can be withdrawn as desired. The advantage of this system is that it yields a quantitative estimate of leachate flux as well as provides a water sample for analysis. The volume of collected leachate per unit area per unit time is an estimate of the downward movement of leachate water at that depth. The major disadvantages to this system are: it is delicate; it requires a trained operator; it estimates leachate quantity somewhat lower than actual field drainage; and it disturbs the soil above the sampler. Further details about the use of the vacuum extractor are given by Trout et al. (1975). Performance of this device when installed in clay soils is generally poor.

Trench Lysimeters

Trench lysimeters are named for the large access trench, or caisson, necessary for operation. Basic installation, as described by Parizek and Lane (1970), involves excavating a rather large trench and shoring up the side walls, taking care to leave open areas so that samplers can be placed in the side walls. Sample trays are imbedded in the side walls and connected by tubing to sample collection containers. The entire trench area is then covered to prevent flooding. One significant danger in using this system is the potential for accumulation of hazardous fumes in the trench, possibly endangering the health and safety of the person collecting the samples.

Trench lysimeters function by intercepting downward-moving water and diverting it into a collection device located at a lower elevation. The intercepting agent may be an open-ended pipe, sheet metal trough, pan, or other similar device. Pans 0.9 to 1.2 m in diameter have been successfully used in the field by Tyler and Thomas (1977). Because there is no vacuum applied to the system, only free water in excess of saturation is sampled. Consequently, samples are plentiful during rainy seasons but are nonexistent during the dry season.

Another variation of this system is to use a funnel filled with clean sand inserted into the sidewall of the trench. Free water will drain into a collection chamber, from which a sample is periodically removed by vacuum. A small sample collection device such as this may be preferable to the large trench because the necessary hole is smaller, so that installation is easier (Figure 9-15).

9.2.2.5 Quality Assurance and Quality Control

Quality assurance (QA) can briefly be defined as the process for ensuring that all data and the decisions based on these data are technically sound, statistically valid, and properly documented. Quality control (QC) procedures are the tools employed to measure the degree to which these quality assurance objectives are met.

A data base cannot be properly evaluated for accuracy and precision unless it is accompanied by quality assurance data. In the case of waste evaluation, these quality assurance data result from the implementation of quality control procedures during sampling and analysis. Quality control requirements for specific analytical methods are given in detail in each method in this manual; in this subsection, quality assurance and quality control procedures for sampling will be discussed.

Quality control procedures that are employed to document the accuracy and precision of sampling are:

1. Trip Blanks: Trip blanks should accompany sample containers to and from the field. These samples can be used to detect any contamination or cross-contamination during handling and transportation.

2. Field Blanks: Field blanks should be collected at specified frequencies, which will vary according to the probability of

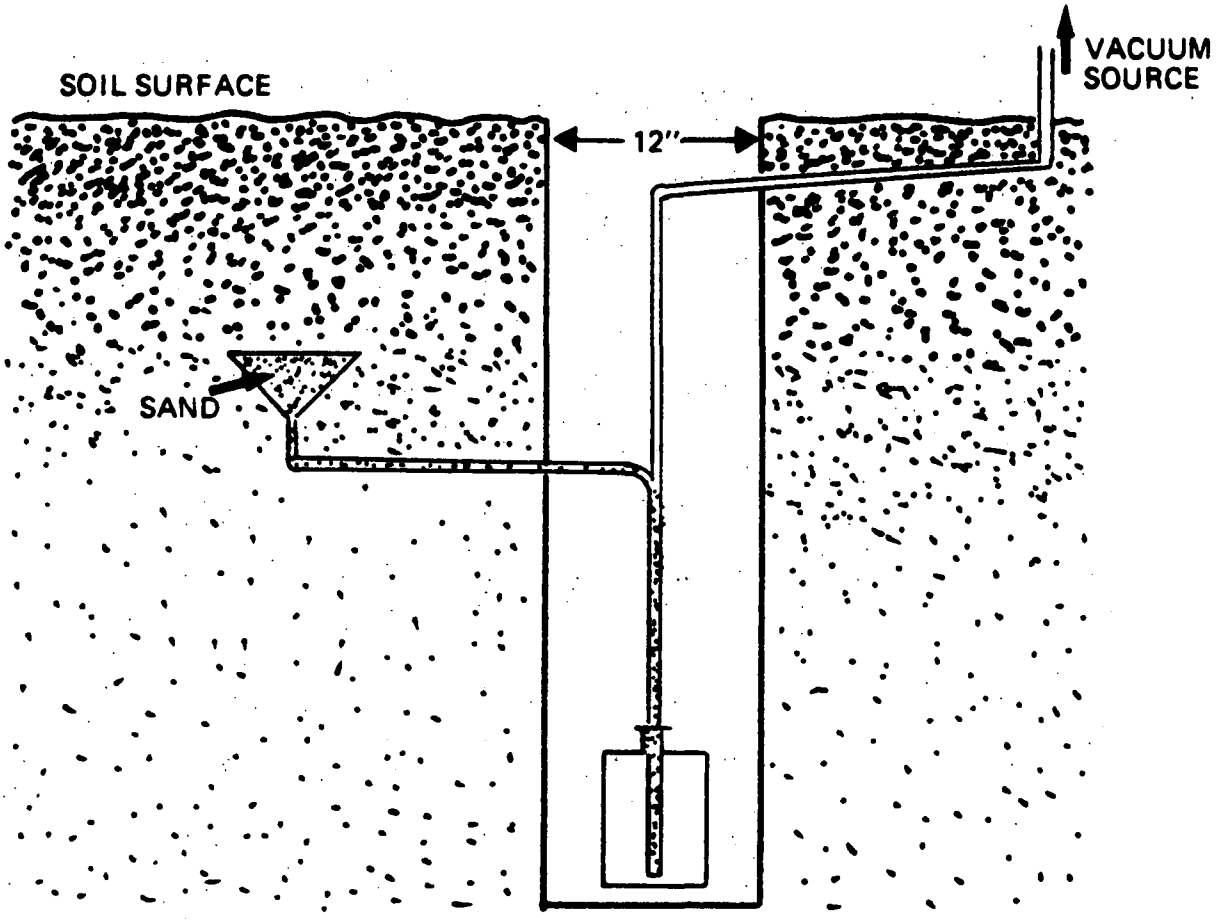


Figure 9-15. Schematic diagram of a sand filled funnel used to collect leachate from the unsaturated zone.

contamination or cross-contamination. Field blanks are often metal- and/or organic-free water aliquots that contact sampling equipment under field conditions and are analyzed to detect any contamination from sampling equipment, cross contamination from previously collected samples, or contamination from conditions during sampling (e.g., airborne contaminants that are not from the waste being sampled).

3. Field Duplicates: Field duplicates are collected at specified frequencies and are employed to document precision. The precision resulting from field duplicates is a function of the variance of waste composition, the variance of the sampling technique, and the variance of the analytical technique.

4. Field Spikes: Field spikes are infrequently used to determine the loss of parameters of interest during sampling and shipment to the laboratories. Because spiking is done in the field, the making of spiked samples or spiked blanks is susceptible to error. In addition, compounds can be lost during spiking, and equipment can be contaminated with spiking solutions. To eliminate these and other problems, some analysts spike blanks or matrices similar to the waste in the laboratory and ship them, along with sample containers, to the field. This approach also has its limitation because the matrix and the handling of the spike are different from those of the actual sample. In all cases, the meaning of a low field-spike recovery is difficult to interpret, and thus, field spikes are not commonly used.

In addition to the above quality control samples, a complete quality assurance program will ensure that standard operating procedures (SOPs) exist for all essential aspects of a sampling effort. SOPs should exist for the following steps in a sampling effort:

1. Definition of objectives (refer to Section 9.2.1).

2. Design of sampling plans (refer to Section 9.2.2).

3. Preparation of containers and equipment (refer to the specific analytical methods).

4. Maintenance, calibration, and cleaning of field equipment (refer to instrument manuals or consult a chemist for cleaning protocols).

5. Sample preservation, packaging, and shipping (refer to the analytical methods and to Section 9.2.2.7).

6. Health and safety protocols (refer to Section 9.2.2.6).

7. Chain-of-custody protocols (refer to Section 9.2.2.7).

In addition to the above protocols, numerous other QA/QC protocols must be employed to document the accuracy of the analytical portion of a waste evaluation program.

9.2.2.6 Health and Safety

Safety and health must also be considered when implementing a sampling plan. A comprehensive health and safety plan has three basic elements: (1) monitoring the health of field personnel; (2) routine safety procedures; and (3) emergency procedures.

Employees who perform field work, as well as those exposed to chemicals in the laboratory, should have a medical examination at the initiation of employment and routinely thereafter. This exam should preferably be performed and evaluated by medical doctors who specialize in industrial medicine. Some examples of parts of a medical examination that ought to be performed are: documentation of medical history; a standard physical exam; pulmonary functions screening; chest X-ray; EKG; urinalysis; and blood chemistry. These procedures are useful to: (1) document the quality of an employee's health at the time of matriculation; (2) ensure the maintenance of good health; and (3) detect early signs of bodily reactions to chemical exposures so they can be treated in a timely fashion. Unscheduled examinations should be performed in the event of an accident, illness, or exposure or suspected exposure to toxic materials.

Regarding safety procedures, personnel should be aware of the common routes of exposure to chemicals (i.e., inhalation, contact, and ingestion) and be instructed in the proper use of safety equipment, such as Draeger tube air samplers to detect air contamination, and in the proper use of protective clothing and respiratory equipment. Protocols should also be defined stating when safety equipment should be employed and designating safe areas where facilities are available for washing, drinking, and eating.

Even when the utmost care is taken, an emergency situation can occur as a result of an unanticipated explosion, electrical hazard, fall, or exposure to a hazardous substance. To minimize the impact of an emergency, field personnel should be aware of basic first aid and have immediate access to a first-aid kit. Phone numbers for both police and the nearest hospital should be obtained and kept by each team member before entering the site. Directions to the nearest hospital should also be obtained so that anyone suffering an injury can be transported quickly for treatment.

9.2.2.7 Chain of Custody

An essential part of any sampling/analytical scheme is ensuring the integrity of the sample from collection to data reporting. The possession and handling of samples should be traceable from the time of collection through analysis and final disposition. This documentation of the history of the sample is referred to as chain of custody.

Chain of custody is necessary if there is any possibility that the analytical data or conclusions based upon analytical data will be used in litigation. In cases where litigation is not involved, many of the chain-of-custody procedures are still useful for routine control of sample flow. The components of chain of custody -- sample seals, a field logbook, chain-of-custody record, and sample analysis request sheet -- and the procedures for their use are described in this section.

A sample is considered is considered to be under a person's custody if it is (1) in a person's physical possession, (2) in view of the person after taking possession, and (3) secured by that person so that no one can tamper with it, or secured by that person in an area that is restricted to authorized personnel. A person who has samples in custody must comply with the following procedures.

(The material presented here briefly summarizes the major aspects of chain of custody. The reader is referred to NEIC Policies and Procedures, EPA-330/9/78/001-R [as revised 1/82], or other manual, as appropriate, for more information.)

Sample labels (Figure 9-16) are necessary to prevent misidentification of samples. Gummed paper labels or tags are adequate and should include at least the following information:

Sample number.
Name of collector.
Date and time of collection.
Place of collection.

Labels should be affixed to sample containers prior to or at the time of sampling and should be filled out at the time of collection.

Sample seals are used to detect unauthorized tampering of samples following sample collection up to the time of analysis. Gummed paper seals may be used for this purpose. The paper seal should include, minimally, the following information:

Sample number. (This number must be identical with the number on the sample label.)
Name of collector.
Date and time of sampling.
Place of collection.

The seal must be attached in such a way that it is necessary to break it in order to open the sample container. (An example of an official sample seal is shown in Figure 9-17.) Seals must be affixed to containers before the samples leave the custody of sampling personnel.

All information pertinent to a field survey or sampling must be recorded in a logbook. This should be bound, preferably with consecutively numbered pages that are 21.6 by 27.9 cm (8-1/2 by 11 in.). At a minimum, entries in the logbook must include the following:

Location of sampling point.
Name and address of field contact.
Producer of waste and address, if different from location.
Type of process producing waste (if known).
Type of waste (e.g., sludge, wastewater).
Suspected waste composition, including concentrations.
Number and volume of sample taken.

Collector _____ Sample No. _____

Place of Collection _____

_____

Date Sampled _____ Time Sampled _____

Field Information _____

_____

_____

Figure 9-16. Example of Sample Label

NAME AND ADDRESS OF ORGANIZATION COLLECTING SAMPLES

Person Collecting Sample _____ Sample No. _____
(signature)

Date Collected _____ Time Collected _____

Place Collected _____

Figure 9-17. Example of Official Sample Seal

Purpose of sampling (e.g., surveillance, contract number).
Description of sampling point and sampling methodology.
Date and time of collection.
Collector's sample identification number(s).
Sample distribution and how transported (e.g., name of laboratory, UPS, Federal Express).
References, such as maps or photographs of the sampling site.
Field observations.
Any field measurements made (e.g., pH, flammability, explosivity).
Signatures of personnel responsible for observations.

Sampling situations vary widely. No general rule can be given as to the extent of information that must be entered in the logbook. A good rule, however, is to record sufficient information so that anyone can reconstruct the sampling without reliance on the collector's memory. The logbook must be stored safely.

To establish the documentation necessary to trace sample possession from the time of collection, a chain-of-custody record should be filled out and should accompany every sample. This record becomes especially important if the sample is to be introduced as evidence in a court litigation. (A chain-of-custody record is illustrated in Figure 9-18.)

The record should contain, minimally, the following information:

Sample number.
Signature of collector.
Date and time of collection.
Place and address of collection.
Waste type.
Signature of persons involved in the chain of possession.
Inclusive dates of possession.

The sample analysis request sheet (Figure 9-19) is intended to accompany the sample on delivery to the laboratory. The field portion of this form is completed by the person collecting the sample and should include most of the pertinent information noted in the logbook. The laboratory portion of this form is intended to be completed by laboratory personnel and to include, minimally:

Name of person receiving the sample.
Laboratory sample number.
Date and time of sample receipt.
Sample allocation.
Analyses to be performed.

The sample should be delivered to the laboratory for analysis as soon as practicable -- usually within 1 or 2 days after sampling. The sample must be accompanied by the chain-of-custody record (Figure 9-18) and by a sample analysis request sheet (Figure 9-19). The sample must be delivered to the person in the laboratory authorized to receive samples (often referred to as the sample custodian).

CHAIN OF CUSTODY RECORD

Proj No.	Project Name												
Samplers *(Signature)*													
Sta. No.	Date	Time	Comp.	Grab	Station Location	No. of Containers							Remarks

Relinquished by: *(Signature)*	Date Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date Time	Received by: *(Signature)*
Relinquished by: *(Signature)*	Date Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date Time	Received by: *(Signature)*
Relinquished by: *(Signature)*	Date Time	Received for Laboratory by: *(Signature)*		Remarks	

Figure 9-18.

SAMPLING ANALYSIS REQUEST

Part I: Field Section

Collector _____ Date Sampled _____ Time _____ hours

Affiliation of Sampler _____

Address _____
number street city state zip

Telephone ( ) _____ Company Contact _____

LABORATORY SAMPLE NUMBER	COLLECTOR'S SAMPLE NO.	TYPE OF SAMPLE*	FIELD INFORMATION**

Analysis Requested _____

_____

_____

Special Handling and/or Storage _____

_____

PART II: LABORATORY SECTION**

Received by _____ Title _____ Date _____

Analysis Required _____

_____

* Indicate whether sample is soil, sludge, etc.
**Use back of page for additional information relative to sample location.

Figure 9-19. Example of hazardous waste sample analysis sheet.

Any material that is identified in the DOT Hazardous Material Table (49 CFR 172.101) must be transported as prescribed in the table. All other hazardous waste samples must be transported as follows:

1. Collect sample in a 16-oz or smaller glass or polyethylene container with nonmetallic Teflon-lined screw cap. For liquids, allow sufficient air space (approximately 10% by volume) so that the container is not full at 54°C (130°F). If collecting a solid material, the container plus contents should not exceed 1 lb net weight. If sampling for volatile organic analysis, fill VOA container to septum but place the VOA container inside a 16-oz or smaller container so that the required air space may be provided. Large quantities, up to 3.785 liters (1 gal), may be collected if the sample's flash point is 23°C (75°F) or higher. In this case, the flash point must be marked on the outside container (e.g., carton or cooler), and shipping papers should state that "Flash point is 73°F or higher."

2. Seal sample and place in a 4-mil-thick polyethylene bag, one sample per bag.

3. Place sealed bag inside a metal can with noncombustible, absorbent cushioning material (e.g., vermiculite or earth) to prevent breakage, one bag per can. Pressure-close the can and use clips, tape, or other positive means to hold the lid securely.

4. Mark the can with:

   Name and address of originator.
   "Flammable Liquid, N.O.S. UN 1993."
   (or, "Flammable Solid, N.O.S. UN 1325".)

NOTE: UN numbers are now required in proper shipping names.

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5. Place one or more metal cans in a strong outside container such as a picnic cooler or fiberboard box. Preservatives are not used for hazardous waste site samples.

6. Prepare for shipping: The words "Flammable Liquid, N.O.S. UN 1993" or "Flammable Solid, N.O.S. UN 1325"; "Cargo Aircraft Only" (if more than 1 qt net per outside package); "Limited Quantity" or "Ltd. Qty."; "Laboratory Samples"; "Net Weight ___" or "Net Volume ___" (of hazardous contents) should be indicated on shipping papers and on the outside of the outside shipping container. The words "This Side Up" or "This End Up" should also be on container. Sign the shipper certification.

7. Stand by for possible carrier requests to open outside containers for inspection or to modify packaging. (It is wise to contact carrier before packing to ascertain local packaging requirements.) Remain in the departure area until the carrier vehicle (aircraft, truck, etc.) is on its way.

At the laboratory, a sample custodian should be assigned to receive the samples. Upon receipt of a sample, the custodian should inspect the condition of the sample and the sample seal, reconcile the information on the sample label and seal against that on the chain-of-custody record, assign a laboratory number, log in the sample in the laboratory logbook, and store it in a secured sample storage room or cabinet until it is assigned to an analyst for analysis.

The sample custodian should inspect the sample for any leakage from the container. A leaky container containing a multiphase sample should not be accepted for analysis. This sample will no longer be a representative sample. If the sample is contained in a plastic bottle and the container walls show that the sample is under pressure or releasing gases, the sample should be treated with caution because it may be explosive or release extremely poisonous gases. The custodian should examine whether the sample seal is intact or broken, because a broken seal may mean sample tampering and would make analysis results inadmissible as evidence in court. Any discrepancies between the information on the sample label and seal and the information that is on the chain-of-custody record and the sample analysis request sheet should be resolved before the sample is assigned for analysis. This effort might require communication with the sample collector. Results of the inspection should be noted on the sample analysis request sheet and on the laboratory sample logbook.

Incoming samples usually carry the inspector's or collector's identification numbers. To identify these samples further, the laboratory should assign its own identification numbers, which normally are given consecutively. Each sample should be marked with the assigned laboratory number. This number is correspondingly recorded on a laboratory sample log book along with the information describing the sample. The sample information is copied from the sample analysis request sheet and cross-checked against that on the sample label.

In most cases, the laboratory supervisor assigns the sample for analysis. The supervisor should review the information on the sample analysis request sheet, which now includes inspection notes recorded by the laboratory sample custodian. The technician assigned to analysis should record in the laboratory notebook the identifying information about the sample, the date of receipt, and other pertinent information. This record should also include the subsequent testing data and calculations. The sample may have to be split with other laboratories in order to obtain all the necessary analytical information. In this case, the same type of chain-of-custody procedures must be employed while the sample is being transported and at the other laboratory.

Once the sample has been received in the laboratory, the supervisor or his/her assignee is responsible for its care and custody. That person should be prepared to testify that the sample was in his/her possession or secured in the laboratory at all times, from the moment it was received from the custodian until the analyses were performed.

9.2.3 Sample Plan Implementation

Prior to implementing a sampling plan, it is often strategic to walk through the sampling plan mentally, starting with the preparation of equipment until the time when samples are received at the laboratory. This mental excursion should be in as much detail as can be imagined, because the small details are the ones most frequently overlooked. By employing this technique, items not included on the equipment list may be discovered, as well as any major oversight that could cause the sampling effort to fail. During this review of the sampling plan, an attempt should be made to anticipate what could go wrong. A solution to anticipated problems should be found, and, if necessary, materials needed for solving these problems should be added to the equipment list.

The remainder of this section discusses examples of sampling strategies for different situations that may be encountered.

Containers

Prior to discussing the sampling of containers, the term must be defined. The term container, as used here, refers to receptacles that are designed for transporting materials, e.g., drums and other smaller receptacles, as opposed to stationary tanks. Weighted bottles, Coliwasas, drum thiefs, or triers are the sampling devices that are chosen for the sampling of containers. (See Section 9.2.2.4 for a full discussion of sampling equipment.)

The sampling strategy for containers varies according to (1) the number of containers to be sampled and (2) access to the containers. Ideally, if the waste is contained in several containers, every container will be sampled. If this is not possible due to the large number of containers or to cost factors, a subset of individual containers must be randomly selected for sampling. This can be done by assigning each container a number and then randomly choosing a set of numbers for sampling.

Access to a container will affect the number of samples that can be taken from the container and the location within the container from which samples can be taken. Ideally, several samples should be taken from locations displaced both vertically and horizontally throughout the waste. The number of samples required for reliable sampling will vary depending on the distribution of the waste components in the container. At a minimum with an unknown waste, a sufficient number and distribution of samples should be taken to address any possible vertical anomalies in the waste. This is because contained wastes have a much greater tendency to be nonrandomly heterogeneous in a vertical rather than a horizontal direction due to (1) settling of solids and the denser phases of liquids and (2) variation in the content of the waste as it enters the container. Bags, paper drums, and open-headed steel drums (of which the entire top can be removed) generally do not restrict access to the waste and therefore do not limit sampling.

When access to a container is unlimited, a useful strategy for obtaining a representative set of samples is a three-dimensional simple random sampling strategy in which the container is divided by constructing an imaginary three-dimensional grid (see Figure 9-20), as follows. First, the top surface of the waste is divided into a grid whose sections either approximate the size of the sampling device or are larger than the sampling device if the container is large. (Cylindrical containers can be divided into imaginary concentric circles, which are then further divided into grids of equal size.) Each section is assigned a number. The height of the container is then divided into imaginary levels that are at least as large as the vertical space required by the chosen sampling device. These imaginary levels are then assigned numbers. Specific levels and grid locations are then selected for sampling using a random-number table or random-number generator. (An alternative means of choosing random sampling locations using circumference and diameter dimensions is discussed in Section 9.2.2.1.)

Another appropriate sampling approach is the two-dimensional simple random sampling strategy, which can usually yield a more precise sampling when fewer samples are collected. This strategy involves (1) dividing the top surface of the waste into an imaginary grid as in the three-dimensional strategy, (2) selecting grid sections for sampling using random-number tables or random-number generators, and (3) sampling each selected grid point in a vertical manner along the entire length from top to bottom using a sampling device such as a drum thief or Coliwasa.

Some containers, such as drums with bung openings, limit access to the contained waste and restrict sampling to a single vertical plane. Samples taken in this manner can be considered representative of the entire container only if the waste is known to be homogeneous or if no horizontal stratification has occurred. Precautions must be taken when sampling any type of steel drum because the drum may explode or expel gases and/or pressurized liquids. An EPA/NEIC manual, "Safety Manual for Hazardous Waste Site Investigation," addresses these safety precautions.

Tanks

Tanks are essentially large containers. The considerations involved in sampling tanks are therefore similar to those for sampling containers. As with containers, the goal of sampling tanks is to acquire a sufficient number of samples from different locations within the waste to provide analytical data that are representative of the entire tank contents.

The accessibility of the tank contents will affect the sampling methodology. If the tank is an open one, allowing unrestricted access, then usually a representative set of samples is best obtained using the three-dimensional simple random sampling strategy, as described for containers (see also Section 9.2.2.1). This strategy involves dividing the tank contents into an imaginary three-dimensional grid. As a first step, the top surface of the waste is divided into a grid whose sections either approximate the size of the sampling device or are larger than the sampling device if the tank is large.

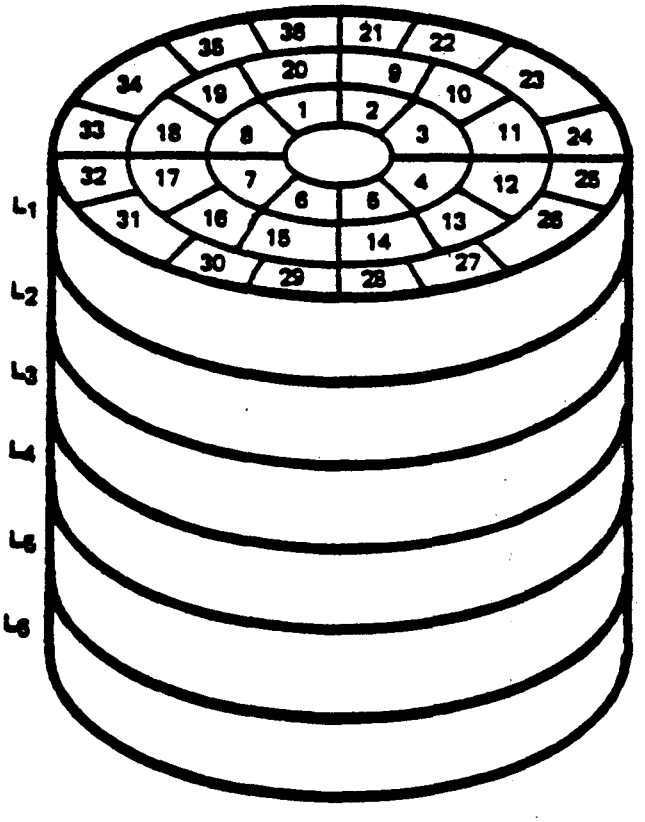

Figure 9-20. Container divided into an imaginary three-dimensional grid.

(Cylindrical tanks can be divided into imaginary concentric circles, which are then further divided into grids of equal size.) Each section is assigned a number. The height of the tank is then divided into imaginary levels that are at least as large as the vertical space required by the chosen sampling device. These imaginary levels are assigned numbers. Specific levels and grid locations are then selected for sampling using a random-number table or random-number generator.

A less comprehensive sampling approach may be appropriate if information regarding the distribution of waste components is known or assumed (e.g., if vertical compositing will yield a representative sample). In such cases, a two-dimensional simple random sampling strategy may be appropriate. In this strategy, the top surface of the waste is divided into an imaginary grid; grid sections are selected using random-number tables or random-number generators; and each selected grid point is then sampled in a vertical manner along the entire length from top to bottom using a sampling device such as a weighted bottle, a drum thief, or Coliwasa. If the waste is known to consist of two or more discrete strata, a more precise representation of the tank contents can be obtained by using a stratified random sampling strategy, i.e., by sampling each stratum separately using the two- or three-dimensional simple random sampling strategy.

Some tanks permit only limited access to their contents, which restricts the locations within the tank from which samples can be taken. If sampling is restricted, the sampling strategy must, at a minimum, take sufficient samples to address the potential vertical anomalies in the waste in order to be considered representative. This is because contained wastes tend to display vertical, rather than horizontal, nonrandom heterogeneity due to settling of suspended solids or denser liquid phases. If access restricts sampling to a portion of the tank contents (e.g., in an open tank, the size of the tank may restrict sampling to the perimeter of the tank; in a closed tank, the only access to the waste may be through inspection ports), then the resulting analytical data will be deemed representative only of the accessed area, not of the entire tank contents unless the tank contents are known to be homogeneous.

If a limited access tank is to be sampled, and little is known about the distribution of components within the waste, a set of samples that is representative of the entire tank contents can be obtained by taking a series of samples as the tank contents are being drained. This should be done in a simple random manner by estimating how long it will take to drain the tank and then randomly selecting times during drainage for sampling.

The most appropriate type of sampling device for tanks depends on the tank parameters. In general, subsurface samplers (i.e., pond samplers) are used for shallow tanks, and weighted bottles are usually employed for tanks deeper than 5 ft. Dippers are useful for sampling pipe effluents.

Waste Piles

In waste piles, the accessibility of waste for sampling is usually a function of pile size, a key factor in the design of a sampling strategy for a waste pile. Ideally, piles containing unknown wastes should be sampled using a three-dimensional simple random sampling strategy. This strategy can be employed only if all points within the pile can be accessed. In such cases, the pile should be divided into a three-dimensional grid system, the grid sections assigned numbers, and the sampling points then chosen using random-number tables or random-number generators.

If sampling is limited to certain portions of the pile, then the collected sample will be representative only of those portions, unless the waste is known to be homogeneous.

In cases where the size of a pile impedes access to the waste, a set of samples that are representative of the entire pile can be obtained with a minimum of effort by scheduling sampling to coincide with pile removal. The number of truckloads needed to remove the pile should be estimated and the truckloads randomly chosen for sampling.

The sampling devices most commonly used for small piles are thiefs, triers, and shovels. Excavation equipment, such as backhoes, can be useful for sampling medium-sized piles.

Landfills and Lagoons

Landfills contain primarily solid waste, whereas lagooned waste may range from liquids to dried sludge residues. Lagooned waste that is either liquid or semisolid is often best sampled using the methods recommended for large tanks. Usually, solid wastes contained in a landfill or lagoon are best sampled using the three-dimensional random sampling strategy.

The three-dimensional random sampling strategy involves establishing an imaginary three-dimensional grid of sampling points in the waste and then using random-number tables or random-number generators to select points for sampling. In the case of landfills and lagoons, the grid is established using a survey or map of the area. The map is divided into two two-dimensional grids with sections of equal size. (An alternative way of choosing random sampling locations is presented in the second example described in Section 9.2.2.1.) These sections are then assigned numbers sequentially.

Next, the depth to which sampling will take place is determined and subdivided into equal levels, which are also sequentially numbered. (The lowest sampling depth will vary from landfill to landfill. Usually, sampling extends to the interface of the fill and the natural soils. If soil contamination is suspected, sampling may extend into the natural soil.) The horizontal and vertical sampling coordinates are then selected using random-number tables or random-number generators. If some information is known about the nature of the waste, then a modified three-dimensional strategy may be more appropriate. For example, if the landfill consists of several cells, a more precise measurement may be obtained by considering each cell as a stratum and employing a stratified three-dimensional random sampling strategy (see Section 9.1).

Hollow-stem augers combined with split-spoon samplers are frequently appropriate for sampling landfills. Water-driven or water-rinsed coring equipment should not be used for sampling because the water can rinse chemical components from the sample. Excavation equipment, such as backhoes, may be useful in obtaining samples at various depths; the resulting holes may be useful for viewing and recording the contents of the landfill.

9.2.4 Sample Compositing

The compositing of samples, is usually done for cost-saving reasons, involves the combining of a number of samples or aliquots of a number of samples collected from the same waste. The disadvantage of sample compositing is the loss of concentration variance data, whereas the advantage is that, for a given analytical cost, a more representative (i.e., more accurate) sample is obtained.

It is usually most expedient and cost effective to collect component samples in the field and to composite aliquots of each sample later in the laboratory. Then, if after reviewing the data any questions arise, the samples can be recomposited in a different combination, or each component sample can be analyzed separately to determine better the variation of waste composition over time and space, or to determine better the precision of an average number. The fact that this recompositing of samples can occur without the need to resample often results in a substantial cost savings.

To ensure that recompositing can be done at a later date, it is essential to collect enough sample volume in the field so that, under normal circumstances, enough component sample will remain following compositing to allow for a different compositing scheme or even for an analysis of the component samples themselves.

The actual compositing of samples requires the homogenization of all component samples to ensure that a representative subsample is aliquoted. The homogenization procedure, and the containers and equipment used for compositing, will vary according to the type of waste being composited and the parameters to be measured. Likewise, the composite sample itself will be homogenized prior to the subsampling of analytical aliquots.

9.2.5 References

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CHAPTER TEN

SAMPLING METHODS

Methods appropriate for use in field sampling situations are included in this chapter. It contains complete sampling methods for a specific purpose. Chapter Nine contains general sampling techniques and plans.

Revision 0
Date September 1986

METHOD 0010

MODIFIED METHOD 5 SAMPLING TRAIN

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of Destruction and Removal Efficiency (DRE) of semivolatile Principal Organic Hazardous Compounds (POHCs) from incineration systems (PHS, 1967). This method also may be used to determine particulate emission rates from stationary sources as per EPA Method 5 (see References at end of this method).

2.0 SUMMARY OF METHOD

2.1 Gaseous and particulate pollutants are withdrawn from an emission source at an isokinetic sampling rate and are collected in a multicomponent sampling train. Principal components of the train include a high-efficiency glass- or quartz-fiber filter and a packed bed of porous polymeric adsorbent resin. The filter is used to collect organic-laden particulate materials and the porous polymeric resin to adsorb semivolatile organic species. Semivolatile species are defined as compounds with boiling points >100°C.

2.2 Comprehensive chemical analyses of the collected sample are conducted to determine the concentration and identity of the organic materials.

3.0 INTERFERENCES

3.1 Oxides of nitrogen (NO_x) are possible interferents in the determination of certain water-soluble compounds such as dioxane, phenol, and urethane; reaction of these compounds with NO_x in the presence of moisture will reduce their concentration. Other possibilities that could result in positive or negative bias are (1) stability of the compounds in methylene chloride, (2) the formation of water-soluble organic salts on the resin in the presence of moisture, and (3) the solvent extraction efficiency of water-soluble compounds from aqueous media. Use of two or more ions per compound for qualitative and quantitative analysis can overcome interference at one mass. These concerns should be addressed on a compound-by-compound basis before using this method.

4.0 APPARATUS AND MATERIALS

4.1 Sampling train:

4.1.1 A schematic of the sampling train used in this method is shown in Figure 1. This sampling train configuration is adapted from EPA Method 5 procedures, and, as such, the majority of the required equipment

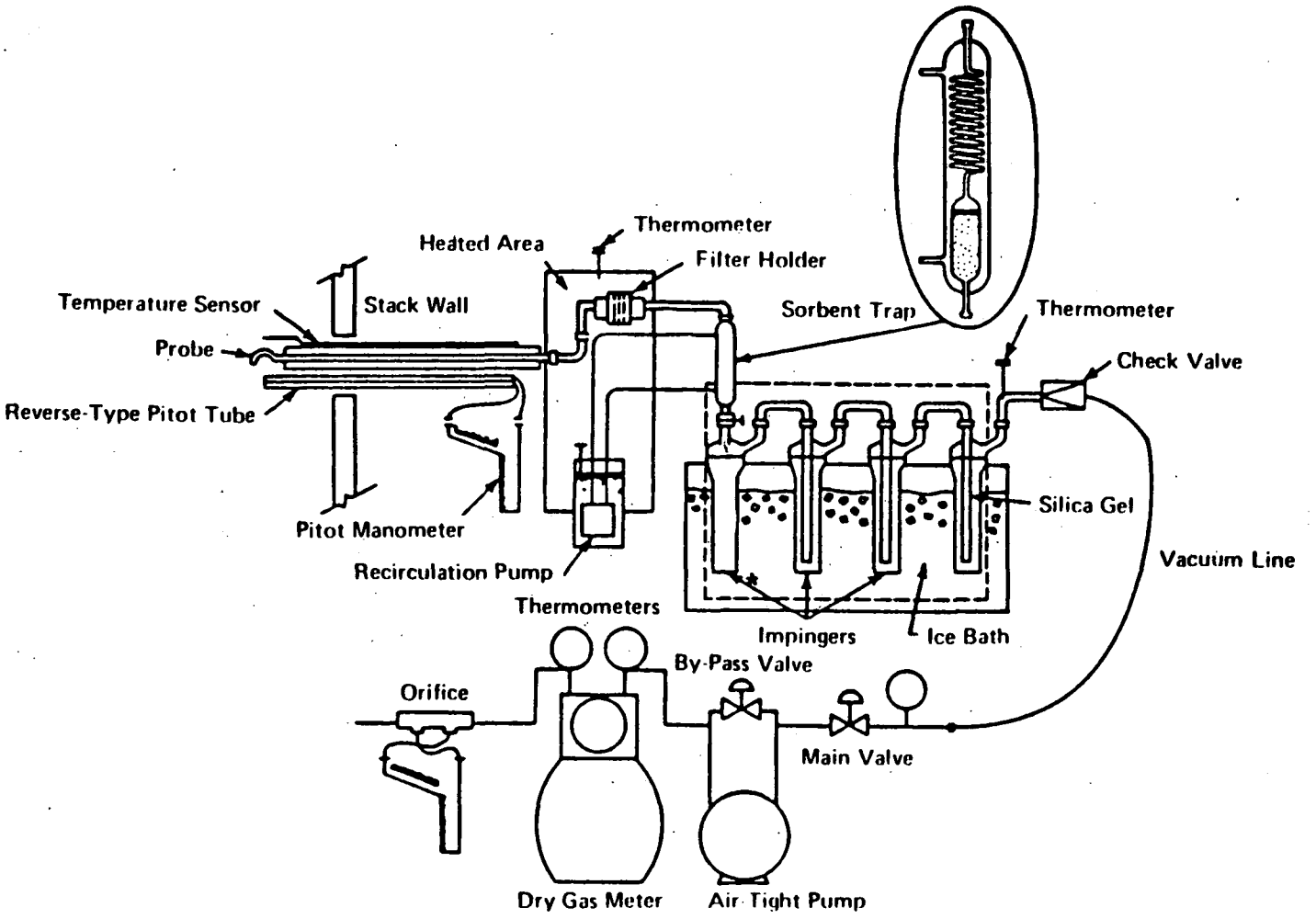

Figure 1. Modified Method 5 Sampling Train.

is identical to that used in EPA Method 5 determinations. The new components required are a condenser coil and a sorbent module, which are used to collect semivolatile organic materials that pass through the glass- or quartz-fiber filter in the gas phase.

4.1.2 Construction details for the basic train components are given in APTD-0581 (see Martin, 1971, in Section 13.0, References); commercial models of this equipment are also available. Specifications for the sorbent module are provided in the following subsections. Additionally, the following subsections list changes to APTD-0581 and identify allowable train configuration modifications.

4.1.3 Basic operating and maintenance procedures for the sampling train are described in APTD-0576 (see Rom, 1972, in Section 13.0, References). As correct usage is important in obtaining valid results, all users should refer to APTD-0576 and adopt the operating and maintenance procedures outlined therein unless otherwise specified. The sampling train consists of the components detailed below.

4.1.3.1 Probe nozzle: Stainless steel (316) or glass with sharp, tapered (30° angle) leading edge. The taper shall be on the outside to preserve a constant I.D. The nozzle shall be buttonhook or elbow design and constructed from seamless tubing (if made of stainless steel). Other construction materials may be considered for particular applications. A range of nozzle sizes suitable for isokinetic sampling should be available in increments of 0.16 cm (1/16 in.), e.g., 0.32-1.27 cm (1/8-1/2 in.), or larger if higher volume sampling trains are used. Each nozzle shall be calibrated according to the procedures outlined in Paragraph 9.1.

4.1.3.2 Probe liner: Borosilicate or quartz-glass tubing with a heating system capable of maintaining a gas temperature of 120 ± 14°C (248 ± 25°F) at the exit end during sampling. (The tester may opt to operate the equipment at a temperature lower than that specified.) Because the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD-0581 and utilizing the calibration curves of APTD-0576 (or calibrated according to the procedure outlined in APTD-0576) are considered acceptable. Either borosilicate or quartz-glass probe liners may be used for stack temperatures up to about 480°C (900°F). Quartz liners shall be used for temperatures between 480 and 900°C (900 and 1650°F). (The softening temperature for borosilicate is 820°C (1508°F), and for quartz 1500°C (2732°F).) Water-cooling of the stainless steel sheath will be necessary at temperatures approaching and exceeding 500°C.

4.1.3.3 Pitot tube: Type S, as described in Section 2.1 of EPA Method 2, or other appropriate devices (Vollaro, 1976). The pitot tube shall be attached to the probe to allow constant monitoring of the stack-gas velocity. The impact (high-pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see EPA Method 2, Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of EPA Method 2.

4.1.3.4 Differential pressure gauge: Inclined manometer or equivalent device as described in Section 2.2 of EPA Method 2. One manometer shall be used for velocity-head (ΔP) readings and the other for orifice differential pressure (ΔH) readings.

4.1.3.5 Filter holder: Borosilicate glass, with a glass frit filter support and a sealing gasket. The sealing gasket should be made of materials that will not introduce organic material into the gas stream at the temperature at which the filter holder will be maintained. The gasket shall be constructed of Teflon or materials of equal or better characteristics. The holder design shall provide a positive seal against leakage at any point along the filter circumference. The holder shall be attached immediately to the outlet of the cyclone or cyclone bypass.

4.1.3.6 Filter heating system: Any heating system capable of maintaining a temperature of 120 $\pm$ 14°C (248 $\pm$ 25°F) around the filter holder during sampling. Other temperatures may be appropriate for particular applications. Alternatively, the tester may opt to operate the equipment at temperatures other than that specified. A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling. Heating systems other than the one shown in APTD-0581 may be used.

4.1.3.7 Organic sampling module: This unit consists of three sections, including a gas-conditioning section, a sorbent trap, and a condensate knockout trap. The gas-conditioning system shall be capable of conditioning the gas leaving the back half of the filter holder to a temperature not exceeding 20°C (68°F). The sorbent trap shall be sized to contain approximately 20 g of porous polymeric resin (Rohm and Haas XAD-2 or equivalent) and shall be jacketed to maintain the internal gas temperature at 17 $\pm$ 3°C (62.5 $\pm$ 5.4°F). The most commonly used coolant is ice water from the impinger ice-water bath, constantly circulated through the outer jacket, using rubber or plastic tubing and a peristaltic pump. The sorbent trap should be outfitted with a glass well or depression, appropriately sized to accommodate a small thermocouple in the trap for monitoring the gas entry temperature. The condensate knockout trap shall be of sufficient size to collect the condensate following gas conditioning. The organic module components shall be oriented to direct the flow of condensate formed vertically downward from the conditioning section, through the adsorbent media, and into the condensate knockout trap. The knockout trap is usually similar in appearance to an empty impinger directly underneath the sorbent module; it may be oversized but should have a shortened center stem (at a minimum, one-half the length of the normal impinger stems) to collect a large volume of condensate without bubbling and overflowing into the impinger train. All surfaces of the organic module wetted by the gas sample shall be fabricated of borosilicate glass, Teflon, or other inert materials. Commercial versions of the

complete organic module are not currently available, but may be assembled from commercially available laboratory glassware and a custom-fabricated sorbent trap. Details of two acceptable designs are shown in Figures 2 and 3 (the thermocouple well is shown in Figure 2).

4.1.3.8 Impinger train: To determine the stack-gas moisture content, four 500-mL impingers, connected in series with leak-free ground-glass joints, follow the knockout trap. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3-cm (1/2-in.) I.D. glass tube extending about 1.3 cm (1/2 in.) from the bottom of the outer cylinder. The second impinger shall be of the Greenburg-Smith design with the standard tip. The first and second impingers shall contain known quantities of water or appropriate trapping solution. The third shall be empty or charged with a caustic solution, should the stack gas contain hydrochloric acid (HCl). The fourth shall contain a known weight of silica gel or equivalent desiccant.

4.1.3.9 Metering system: The necessary components are a vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), dry-gas meter capable of measuring volume to within 1%, and related equipment, as shown in Figure 1. At a minimum, the pump should be capable of 4 cfm free flow, and the dry-gas meter should have a recording capacity of 0-999.9 cu ft with a resolution of 0.005 cu ft. Other metering systems capable of maintaining sampling rates within 10% of isokineticity and of determining sample volumes to within 2% may be used. The metering system must be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates. Sampling trains using metering systems designed for flow rates higher than those described in APTD-0581 and APTD-0576 may be used, provided that the specifications of this method are met.

4.1.3.10 Barometer: Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases the barometric reading may be obtained from a nearby National Weather Service station, in which case the station value (which is the absolute barometric pressure) is requested and an adjustment for elevation differences between the weather station and sampling point is applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30-m (100 ft) elevation increase (vice versa for elevation decrease).

4.1.3.11 Gas density determination equipment: Temperature sensor and pressure gauge (as described in Sections 2.3 and 2.4 of EPA Method 2), and gas analyzer, if necessary (as described in EPA Method 3). The temperature sensor ideally should be permanently attached to the pitot tube or sampling probe in a fixed configuration such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal.

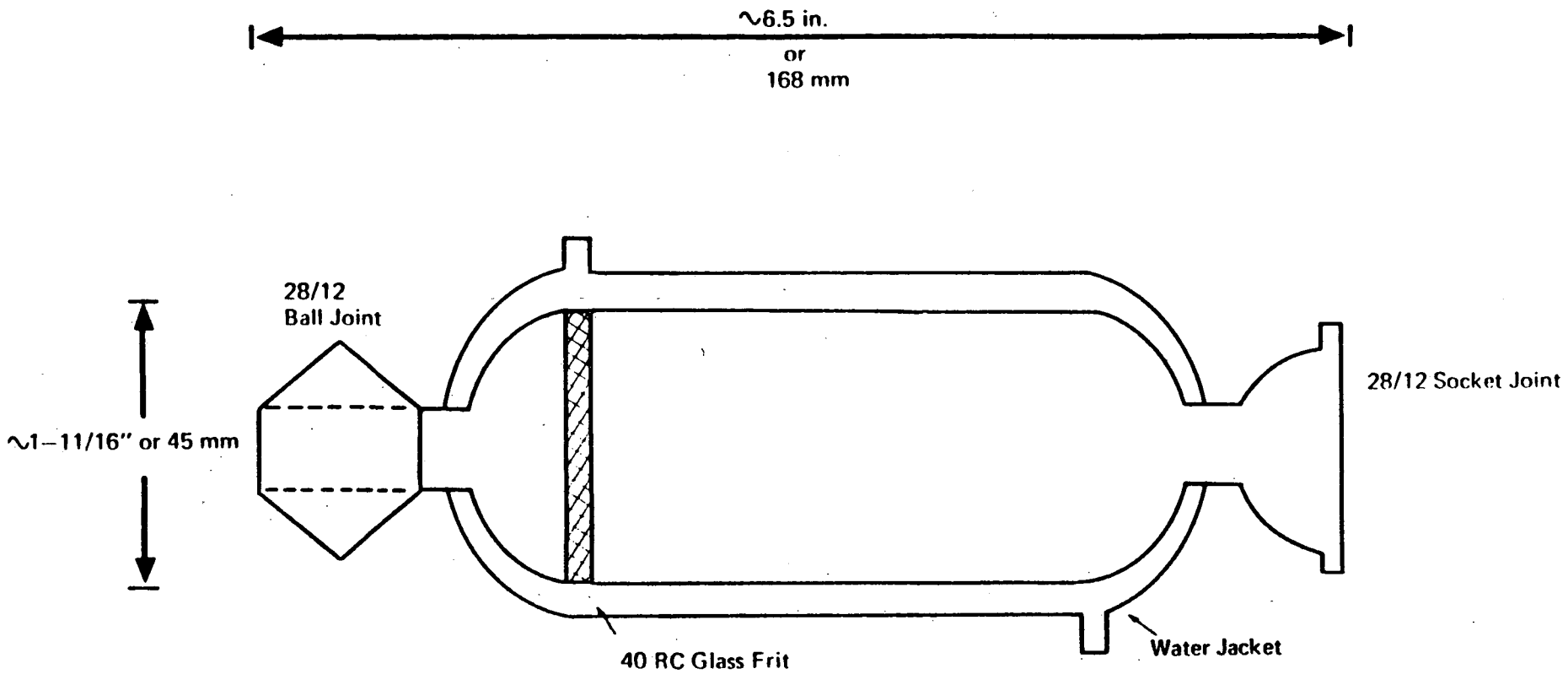

Figure 2. Adsorbent Sampling System.

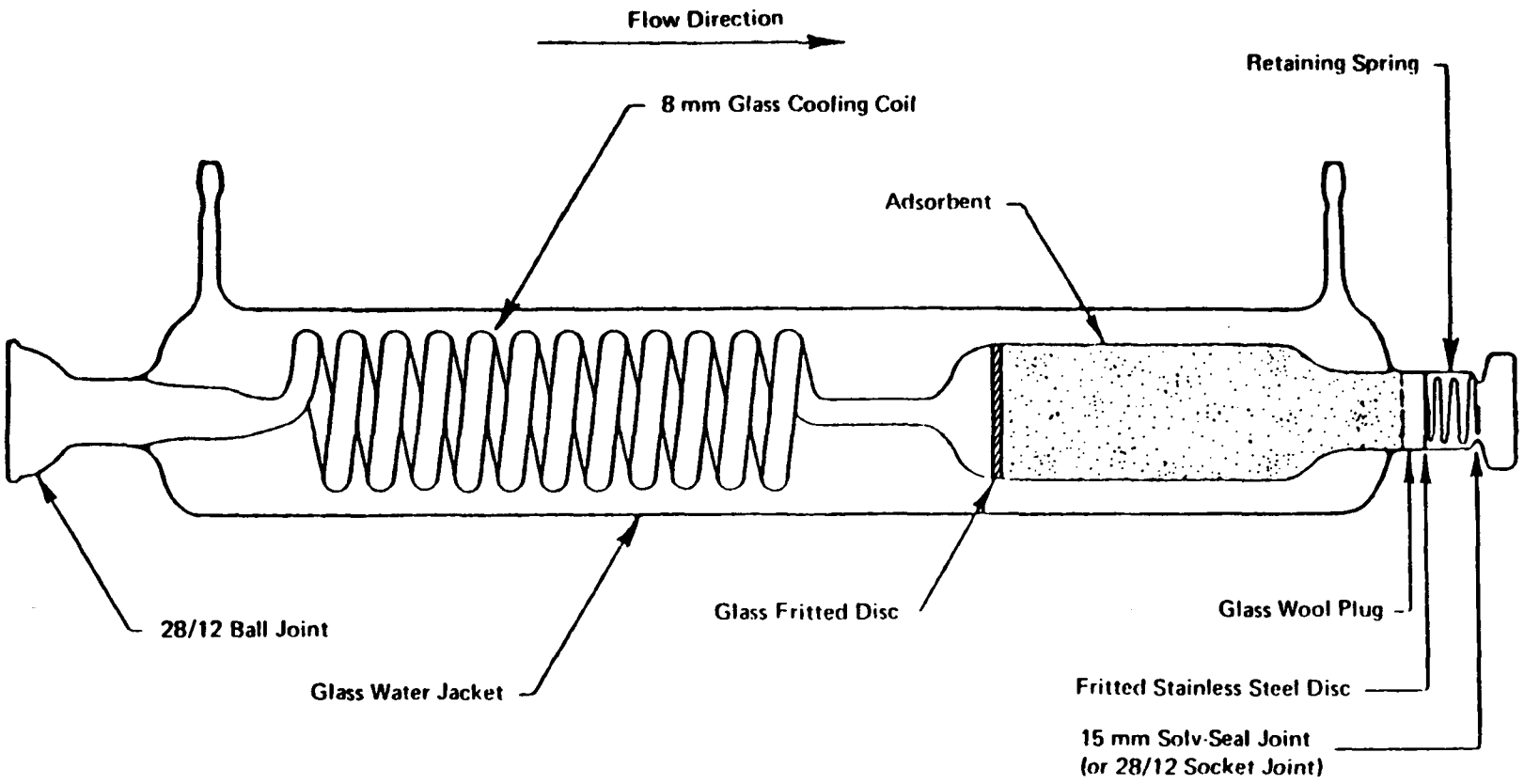

Figure 3. Adsorbent Sampling System.

Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see EPA Method 2, Figure 2-7). As a second alternative, if a difference of no more than 1% in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pitot tube.

4.1.3.12 Calibration/field-preparation record: A permanently bound laboratory notebook, in which duplicate copies of data may be made as they are being recorded, is required for documenting and recording calibrations and preparation procedures (i.e., filter and silica gel tare weights, clean XAD-2, quality assurance/quality control check results, dry-gas meter, and thermocouple calibrations, etc.). The duplicate copies should be detachable and should be stored separately in the test program archives.

4.2 Sample Recovery:

4.2.1 **Probe liner:** Probe nozzle and organic module conditioning section brushes; nylon bristle brushes with stainless steel wire handles are required. The probe brush shall have extensions of stainless steel, Teflon, or inert material at least as long as the probe. The brushes shall be properly sized and shaped to brush out the probe liner, the probe nozzle, and the organic module conditioning section.

4.2.2 **Wash bottles:** Three. Teflon or glass wash bottles are recommended; polyethylene wash bottles should not be used because organic contaminants may be extracted by exposure to organic solvents used for sample recovery.

4.2.3 **Glass sample storage containers:** Chemically resistant, borosilicate amber and clear glass bottles, 500-mL or 1,000-mL. Bottles should be tinted to prevent action of light on sample. Screw-cap liners shall be either Teflon or constructed so as to be leak-free and resistant to chemical attack by organic recovery solvents. Narrow-mouth glass bottles have been found to exhibit less tendency toward leakage.

4.2.4 **Petri dishes:** Glass, sealed around the circumference with wide (1-in.) Teflon tape, for storage and transport of filter samples.

4.2.5 **Graduated cylinder and/or balances:** To measure condensed water to the nearest 1 mL or 1 g. Graduated cylinders shall have subdivisions not >2 mL. Laboratory triple-beam balances capable of weighing to ± 0.5 g or better are required.

4.2.6 **Plastic storage containers:** Screw-cap polypropylene or polyethylene containers to store silica gel.

4.2.7 **Funnel and rubber policeman:** To aid in transfer of silica gel to container (not necessary if silica gel is weighed in field).

4.2.8 **Funnels:** Glass, to aid in sample recovery.

4.3 Filters: Glass- or quartz-fiber filters, without organic binder, exhibiting at least 99.95% efficiency (<0.05% penetration) on 0.3-um dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D2986-71. Test data from the supplier's quality control program are sufficient for this purpose. In sources containing SO_2 or SO_3, the filter material must be of a type that is unreactive to SO_2 or SO_3. Reeve Angel 934 AH or Schleicher and Schwell #3 filters work well under these conditions.

4.4 Crushed ice: Quantities ranging from 10-50 lb may be necessary during a sampling run, depending on ambient air temperature.

4.5 Stopcock grease: Solvent-insoluble, heat-stable silicone grease. Use of silicone grease upstream of the module is not permitted, and amounts used on components located downstream of the organic module shall be minimized. Silicone grease usage is not necessary if screw-on connectors and Teflon sleeves or ground-glass joints are used.

4.6 Glass wool: Used to plug the unfritted end of the sorbent module. The glass-wool fiber should be solvent-extracted with methylene chloride in a Soxhlet extractor for 12 hr and air-dried prior to use.

5.0 REAGENTS

5.1 Adsorbent resin: Porous polymeric resin (XAD-2 or equivalent) is recommended. These resins shall be cleaned prior to their use for sample collection. Appendix A of this method should be consulted to determine appropriate precleaning procedure. For best results, resin used should not exhibit a blank of higher than 4 mg/kg of total chromatographable organics (TCO) (see Appendix B) prior to use. Once cleaned, resin should be stored in an airtight, wide-mouth amber glass container with a Teflon-lined cap or placed in one of the glass sorbent modules tightly sealed with Teflon film and elastic bands. The resin should be used within 4 wk of the preparation.

5.2 Silica gel: Indicating type, 6-16 mesh. If previously used, dry at 175°C (350°F) for 2 hr before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

5.3 Impinger solutions: Distilled organic-free water (Type II) shall be used, unless sampling is intended to quantify a particular inorganic gaseous species. If sampling is intended to quantify the concentration of additional species, the impinger solution of choice shall be subject to Administrator approval. This water should be prescreened for any compounds of interest. One hundred mL will be added to the specified impinger; the third impinger in the train may be charged with a basic solution (1 N sodium hydroxide or sodium acetate) to protect the sampling pump from acidic gases. Sodium acetate should be used when large sample volumes are anticipated because sodium hydroxide will react with carbon dioxide in aqueous media to form sodium carbonate, which may possibly plug the impinger.

5.4 Sample recovery reagents:

5.4.1 **Methylene chloride:** Distilled-in-glass grade is required for sample recovery and cleanup (see Note to 5.4.2 below).

5.4.2 **Methyl alcohol:** Distilled-in-glass grade is required for sample recovery and cleanup.

NOTE: Organic solvents from metal containers may have a high residue blank and should not be used. Sometimes suppliers transfer solvents from metal to glass bottles; thus blanks shall be run prior to field use and only solvents with low blank value (<0.001%) shall be used.

5.4.3 **Water:** Water (Type II) shall be used for rinsing the organic module and condenser component.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Because of complexity of this method, field personnel should be trained in and experienced with the test procedures in order to obtain reliable results.

6.2 Laboratory preparation:

6.2.1 All the components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified.

6.2.2 Weigh several 200- to 300-g portions of silica gel in airtight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus containers. As an alternative to preweighing the silica gel, it may instead be weighed directly in the impinger or sampling holder just prior to train assembly.

6.2.3 Check filters visually against light for irregularities and flaws or pinhole leaks. Label the shipping containers (glass Petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

6.2.4 Desiccate the filters at 20 ± 5.6°C (68 ± 10°F) and ambient pressure for at least 24 hr, and weigh at intervals of at least 6 hr to a constant weight (i.e., <0.5-mg change from previous weighing), recording results to the nearest 0.1 mg. During each weighing the filter must not be exposed for more than a 2-min period to the laboratory atmosphere and relative humidity above 50%. Alternatively (unless otherwise specified by the Administrator), the filters may be oven-dried at 105°C (220°F) for 2-3 hr, desiccated for 2 hr, and weighed.

6.3 Preliminary field determinations:

6.3.1 Select the sampling site and the minimum number of sampling points according to EPA Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and range of velocity heads using EPA Method 2. It is recommended that a leak-check of the pitot lines (see EPA Method 2, Section 3.1) be performed. Determine the stack-gas moisture content using EPA Approximation Method 4 or its alternatives to establish estimates of isokinetic sampling-rate settings. Determine the stack-gas dry molecular weight, as described in EPA Method 2, Section 3.6. If integrated EPA Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

6.3.2 Select a nozzle size based on the range of velocity heads so that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of EPA Method 2).

6.3.3 Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, to reduce the length of the probe, consider sampling from opposite sides of the stack.

6.3.4 A minimum of 3 dscm (105.9 dscf) of sample volume is required for the determination of the Destruction and Removal Efficiency (DRE) of POHCs from incineration systems. Additional sample volume shall be collected as necessitated by analytical detection limit constraints. To determine the minimum sample volume required, refer to sample calculations in Section 10.0.

6.3.5 Determine the total length of sampling time needed to obtain the identified minimum volume by comparing the anticipated average sampling rate with the volume requirement. Allocate the same time to all traverse points defined by EPA Method 1. To avoid timekeeping errors, the length of time sampled at each traverse point should be an integer or an integer plus one-half min.

6.3.6 In some circumstances (e.g., batch cycles) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas-sample volumes. In these cases, the Administrator's approval must first be obtained.

6.4 Preparation of collection train:

6.4.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered with Teflon film or aluminum foil until just prior to assembly or until sampling is about to begin.

6.4.2 Fill the sorbent trap section of the organic module with approximately 20 g of clean adsorbent resin. While filling, ensure that the trap packs uniformly, to eliminate the possibility of channeling. When freshly cleaned, many adsorbent resins carry a static charge, which will cause clinging to trap walls. This may be minimized by filling the trap in the presence of an antistatic device. Commercial antistatic devices include Model-204 and Model-210 manufactured by the 3M Company, St. Paul, Minnesota.

6.4.3 If an impinger train is used to collect moisture, place 100 mL of water in each of the first two impingers, leave the third impinger empty (or charge with caustic solution, as necessary), and transfer approximately 200-300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

6.4.4 Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

6.4.5 When glass liners are used, install the selected nozzle using a Viton-A O-ring when stack temperatures are <260°C (500°F) and a woven glass-fiber gasket when temperatures are higher. See APTD-0576 (Rom, 1972) for details. Other connecting systems utilizing either 316 stainless steel or Teflon ferrules may be used. When metal liners are used, install the nozzle as above, or by a leak-free direct mechanical connection. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

6.4.6 Set up the train as in Figure 1. During assembly, do not use any silicone grease on ground-glass joints that are located upstream of the organic module. A very light coating of silicone grease may be used on all ground-glass joints that are located downstream of the organic module, but it should be limited to the outer portion (see APTD-0576) of the ground-glass joints to minimize silicone-grease contamination. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and the filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack. The organic module condenser must be maintained at a temperature of 17 ± 3°C. Connect all temperature sensors to an appropriate potentiometer/display unit. Check all temperature sensors at ambient temperature.

6.4.7 Place crushed ice around the impingers and the organic module condensate knockout.

6.4.8 Turn on the sorbent module and condenser coil coolant recirculating pump and begin monitoring the sorbent module gas entry temperature. Ensure proper sorbent module gas entry temperature before proceeding and again before any sampling is initiated. It is extremely important that the XAD-2 resin temperature never exceed 50°C (122°F), because thermal decomposition will occur. During testing, the XAD-2 temperature must not exceed 20°C (68°F) for efficient capture of the semivolatile species of interest.

6.4.9 Turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize.

6.5 Leak-check procedures

6.5.1 **Pre-test leak-check:**

6.5.1.1 Because the number of additional intercomponent connections in the Semi-VOST train (over the M5 Train) increases the possibility of leakage, a pre-test leak-check is required.

6.5.1.2 After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 381-mm Hg (15-in. Hg) vacuum.
(NOTE: A lower vacuum may be used, provided that it is not exceeded during the test.)

6.5.1.3 If an asbestos string is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first attaching a carbon-filled leak-check impinger (shown in Figure 4) to the inlet of the filter holder (cyclone, if applicable) and then plugging the inlet and pulling a 381-mm Hg (15-in. Hg) vacuum. (Again, a lower vacuum may be used, provided that it is not exceeded during the test.) Then, connect the probe to the train and leak-check at about 25-mm Hg (1-in. Hg) vacuum; alternatively, leak-check the probe with the rest of the sampling train in one step at 381-mm Hg (15-in. Hg) vacuum. Leakage rates in excess of 4% of the average sampling rate or >0.00057 m^3/min (0.02 cfm), whichever is less, are unacceptable.

6.5.1.4 The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with fine-adjust valve fully open and coarse-adjust valve completely closed. Partially open the coarse-adjust valve and slowly close the fine-adjust valve until the desired vacuum is reached. Do not reverse direction of the fine-adjust valve; this will cause water to back up into the organic module. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check, as shown below, and start over.

CROSS SECTIONAL VIEW

Leak Testing Apparatus

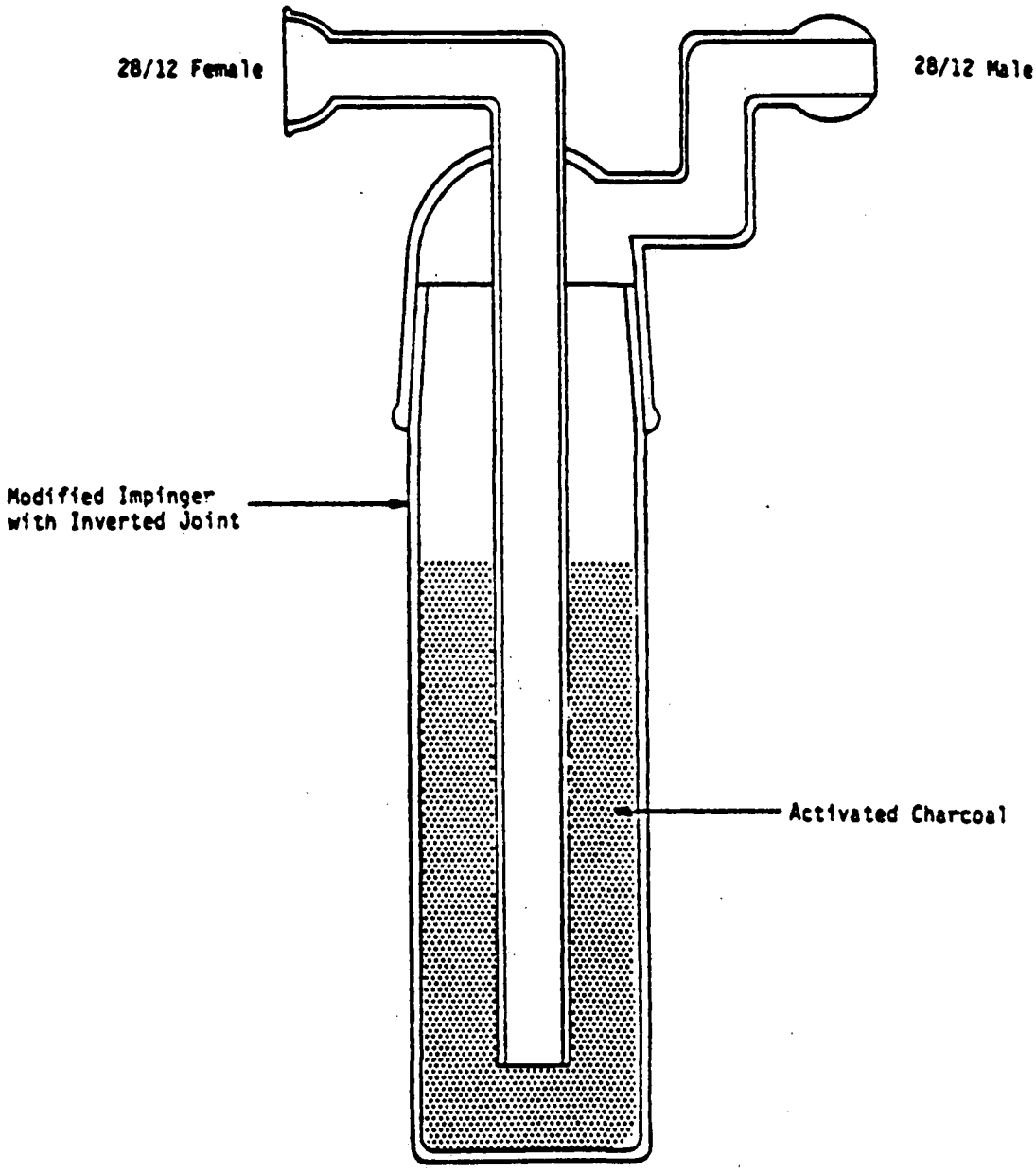

Figure 4. Leak-check impinger.

6.5.1.5 When the leak-check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable). When the vacuum drops to 127 mm (5 in.) Hg or less, immediately close the coarse-adjust valve. Switch off the pumping system and reopen the fine-adjust valve. Do not reopen the fine-adjust valve until the coarse-adjust valve has been closed. This prevents the water in the impingers from being forced backward into the organic module and silica gel from being entrained backward into the third impinger.

6.5.2 **Leak-checks during sampling run:**

6.5.2.1 If, during the sampling run, a component (e.g., filter assembly, impinger, or sorbent trap) change becomes necessary, a leak-check shall be conducted immediately after the interruption of sampling and before the change is made. The leak-check shall be done according to the procedure outlined in Paragraph 6.5.1, except that it shall be done at a vacuum greater than or equal to the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered. If a higher leakage rate is obtained, the tester shall void the sampling run. (It should be noted that any "correction" of the sample volume by calculation by calculation reduces the integrity of the pollutant concentrations data generated and must be avoided.)

6.5.2.2 Immediately after a component change, and before sampling is reinitiated, a leak-check similar to a pre-test leak-check must also be conducted.

6.5.3 **Post-test leak-check:**

6.5.3.1 A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done with the same procedures as those with the pre-test leak-check, except that it shall be conducted at a vacuum greater than or equal to the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate, correct the sample volume (as shown in the calculation section of this method), and consider the data obtained of questionable reliability, or void the sampling run.

6.6 Sampling-train operation:

6.6.1 During the sampling run, maintain an isokinetic sampling rate to within 10% of true isokinetic, unless otherwise specified by the Administrator. Maintain a temperature around the filter of 120 ± 14°C (248 ± 25°F) and a gas temperature entering the sorbent trap at a maximum of 20°C (68°F).

6.6.2 For each run, record the data required on a data sheet such as the one shown in Figure 5. Be sure to record the initial dry-gas meter reading. Record the dry-gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made before and after each leak-check, and when sampling is halted. Take other readings required by Figure 5 at least once at each sample point during each time increment and additional readings when significant changes (20% variation in velocity-head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

6.6.3 Clean the stack access ports prior to the test run to eliminate the chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe heating systems are at the specified temperature, and verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point, with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations, are available. These nomographs are designed for use when the Type S pitot-tube coefficient is 0.84 $\pm$ 0.02 and the stack-gas equivalent density (dry molecular weight) is equal to 29 $\pm$ 4. APTD-0576 details the procedure for using the nomographs. If the stack-gas molecular weight and the pitot-tube coefficient are outside the above ranges, do not use the nomographs unless appropriate steps (Shigehara, 1974) are taken to compensate for the deviations.

6.6.4 When the stack is under significant negative pressure (equivalent to the height of the impinger stem), take care to close the coarse-adjust valve before inserting the probe into the stack, to prevent water from backing into the organic module. If necessary, the pump may be turned on with the coarse-adjust valve closed.

6.6.5 When the probe is in position, block off the openings around the probe and stack access port to prevent unrepresentative dilution of the gas stream.

6.6.6 Traverse the stack cross section, as required by EPA Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the access port, in order to minimize the chance of extracting deposited material.

6.6.7 During the test run, make periodic adjustments to keep the temperature around the filter holder and the organic module at the proper levels; add more ice and, if necessary, salt to maintain a temperature of <20°C (68°F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

Plant _____
Location _____
Operator _____
Date _____
Run No. _____
Sample Box No. _____
Meter Box No. _____
Meter H@ _____
C Factor _____
Pitot Tube Coefficient C_p _____

Schematic of Stack Cross Section

Ambient Temperature _____
Barometric Pressure _____
Assumed Moisture % _____
Probe Length, m (ft) _____
Nozzle Identification No. _____
Average Calibrated Nozzle Diameter, cm (in) _____
Probe Heater Setting _____
Leak Rate, m^3/min, (cfm) _____
Probe Liner Material _____
Static Pressure, mm Hg (in. Hg) _____
Filter No. _____

Traverse Point Number	Sampling Time (8) min.	Vacuum mm Hg (in. Hg)	Stack Temperature (T_S) °C(°F)	Velocity Head (P_S) mm (in) H_2O	Pressure Differential Across Orifice Meter mm (H_2O) (in H_2O)	Gas Sample Volume m_3 (ft_3)	Gas Sample Temp. at Dry Gas Meter Inlet °C(°F)	Gas Sample Temp. at Dry Gas Meter Outlet °C(F°)	Filter Holder Temperature °C(F°)	Temperature of Gas Leaving Condenser or Last Impinger °C(F°)	Temperature of Gas Entering Sorbet Trap °C(F°)
Total							Avg.	Avg.			
Average											

Figure 5. Particulate field data.

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6.6.8 If the pressure drop across the filter or sorbent trap becomes too high, making isokinetic sampling difficult to maintain, the filter/sorbent trap may be replaced in the midst of a sample run. Using another complete filter holder/sorbent trap assembly is recommended, rather than attempting to change the filter and resin themselves. After a new filter/sorbent trap assembly is installed, conduct a leak-check. The total particulate weight shall include the summation of all filter assembly catches.

6.6.9 A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

6.6.10 Note that when two or more trains are used, separate analysis of the front-half (if applicable) organic-module and impinger (if applicable) catches from each train shall be performed, unless identical nozzle sizes were used on all trains. In that case, the front-half catches from the individual trains may be combined (as may the impinger catches), and one analysis of front-half catch and one analysis of impinger catch may be performed.

6.6.11 At the end of the sample run, turn off the coarse-adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry-gas meter reading, and conduct a post-test leak-check. Also, leak-check the pitot lines as described in EPA Method 2. The lines must pass this leak-check in order to validate the velocity-head data.

6.6.12 Calculate percent isokineticity (see Section 10.8) to determine whether the run was valid or another test run should be made.

7.0 SAMPLE RECOVERY

7.1 Preparation:

7.1.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over the tip to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling down because this will create a vacuum in the filter holder, drawing water from the impingers into the sorbent module.

7.1.2 Before moving the sample train to the cleanup site, remove the probe from the sample train and cap the open outlet, being careful not to lose any condensate that might be present. Cap the filter inlet.

Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the organic module and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the organic module.

7.1.3 Cap the filter-holder outlet and the inlet to the organic module. Separate the sorbent trap section of the organic module from the condensate knockout trap and the gas-conditioning section. Cap all organic module openings. Disconnect the organic-module knockout trap from the impinger train inlet and cap both of these openings. Ground-glass stoppers, Teflon caps, or caps of other inert materials may be used to seal all openings.

7.1.4 Transfer the probe, the filter, the organic-module components, and the impinger/condenser assembly to the cleanup area. This area should be clean and protected from the weather to minimize sample contamination or loss.

7.1.5 Save a portion of all washing solutions (methanol/methylene chloride, Type II water) used for cleanup as a blank. Transfer 200 mL of each solution directly from the wash bottle being used and place each in a separate, prelabeled glass sample container.

7.1.6 Inspect the train prior to and during disassembly and note any abnormal conditions.

7.2 Sample containers:

7.2.1 **Container no. 1:** Carefully remove the filter from the filter holder and place it in its identified Petri dish container. Use a pair or pairs of tweezers to handle the filter. If it is necessary to fold the filter, ensure that the particulate cake is inside the fold. Carefully transfer to the Petri dish any particulate matter or filter fibers that adhere to the filter-holder gasket, using a dry nylon bristle brush or sharp-edged blade, or both. Label the container and seal with 1-in.-wide Teflon tape around the circumference of the lid.

7.2.2 **Container no. 2:** Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components first with methanol/methylene chloride (1:1 v/v) into a glass container. Distilled water may also be used. Retain a water and solvent blank and analyze in the same manner as with the samples. Perform rinses as follows:

7.2.2.1 Carefully remove the probe nozzle and clean the inside surface by rinsing with the solvent mixture (1:1 v/v methanol/-methylene chloride) from a wash bottle and brushing with a nylon bristle brush. Brush until the rinse shows no visible particles; then make a final rinse of the inside surface with the solvent mix. Brush and rinse the inside parts of the Swagelok fitting with the solvent mix in a similar way until no visible particles remain.

7.2.2.2 Have two people rinse the probe liner with the solvent mix by tilting and rotating the probe while squirting solvent into its upper end so that all inside surfaces will be wetted with solvent. Let the solvent drain from the lower end into the sample container. A glass funnel may be used to aid in transferring liquid washes to the container.

7.2.2.3 Follow the solvent rinse with a probe brush. Hold the probe in an inclined position and squirt solvent into the upper end while pushing the probe brush through the probe with a twisting action; place a sample container underneath the lower end of the probe and catch any solvent and particulate matter that is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the solvent or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above-prescribed manner at least six times (metal probes have small crevices in which particulate matter can be entrapped). Rinse the brush with solvent and quantitatively collect these washings in the sample container. After the brushing, make a final solvent rinse of the probe as described above.

7.2.2.4 It is recommended that two people work together to clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

7.2.2.5 Clean the inside of the front half of the filter holder and cyclone/cyclone flask, if used, by rubbing the surfaces with a nylon bristle brush and rinsing with methanol/methylene chloride (1:1 v/v) mixture. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone and cyclone flask (if applicable). Brush and rinse any particulate material adhering to the inner surfaces of these components into the front-half rinse sample. After all solvent washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that solvent will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to identify its contents.

7.2.3 **Container no. 3:** The sorbent trap section of the organic module may be used as a sample transport container, or the spent resin may be transferred to a separate glass bottle for shipment. If the sorbent trap itself is used as the transport container, both ends should be sealed with tightly fitting caps or plugs. Ground-glass stoppers or Teflon caps may be used. The sorbent trap should then be labeled, covered with aluminum foil, and packaged on ice for transport to the laboratory. If a separate bottle is used, the spent resin should be quantitatively transferred from the trap into the clean bottle. Resin that adheres to the walls of the trap should be recovered using a rubber policeman or spatula and added to this bottle.

7.2.4 **Container no. 4:** Measure the volume of condensate collected in the condensate knockout section of the organic module to within ±1 mL by using a graduated cylinder or by weighing to within ±0.5 g using a triple-beam balance. Record the volume or weight of liquid present and note any discoloration or film in the liquid catch. Transfer this liquid to a prelabeled glass sample container. Inspect the back half of the filter housing and the gas-conditioning section of the organic module. If condensate is observed, transfer it to a graduated or weighing bottle and measure the volume, as described above. Add this material to the condensate knockout-trap catch.

7.2.5 **Container no. 5:** All sampling train components located between the high-efficiency glass- or quartz-fiber filter and the first wet impinger or the final condenser system (including the heated Teflon line connecting the filter outlet to the condenser) should be thoroughly rinsed with methanol/methylene chloride (1:1 v/v) and the rinsings combined. This rinse shall be separated from the condensate. If the spent resin is transferred from the sorbent trap to a separate sample container for transport, the sorbent trap shall be thoroughly rinsed until all sample-wetted surfaces appear clean. Visible films should be removed by brushing. Whenever train components are brushed, the brush should be subsequently rinsed with solvent mixture and the rinsings added to this container.

7.2.6 **Container no. 6:** Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere strongly to the impinger wall. Because the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, weigh the container and its contents to 0.5 g or better.

7.3 Impinger water:

7.3.1 Make a notation of any color or film in the liquid catch. Measure the liquid in the first three impingers to within ±1 mL by using a graduated cylinder or by weighing it to within ±0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

7.3.2 Discard the liquid after measuring and recording the volume or weight, unless analysis of the impinger catch is required (see Paragraph 4.1.3.7). Amber glass containers should be used for storage of impinger catch, if required.

7.3.3 If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically.

7.4 Sample preparation for shipment: Prior to shipment, recheck all sample containers to ensure that the caps are well secured. Seal the lids of all containers around the circumference with Teflon tape. Ship all liquid samples upright on ice and all particulate filters with the particulate catch facing upward. The particulate filters should be shipped unrefrigerated.

8.0 ANALYSIS

8.1 Sample preparation:

8.1.1 **General:** The preparation steps for all samples will result in a finite volume of concentrated solvent. The final sample volume (usually in the 1- to 10-mL range) is then subjected to analysis by GC/MS. All samples should be inspected and the appearance documented. All samples are to be spiked with surrogate standards as received from the field prior to any sample manipulations. The spike should be at a level equivalent to 10 times the MDL when the solvent is reduced in volume to the desired level (i.e., 10 mL). The spiking compounds should be the stable isotopically labeled analog of the compounds of interest or a compound that would exhibit properties similar to the compounds of interest, be easily chromatographed, and not interfere with the analysis of the compounds of interest. Suggested surrogate spiking compounds are: deuterated naphthalene, chrysene, phenol, nitrobenzene, chlorobenzene, toluene, and carbon-13-labeled pentachlorophenol.

8.1.2 **Condensate:** The "condensate" is the moisture collected in the first impinger following the XAD-2 module. Spike the condensate with the surrogate standards. The volume is measured and recorded and then transferred to a separatory funnel. The pH is to be adjusted to pH 2 with 6 N sulfuric acid, if necessary. The sample container and graduated cylinder are sequentially rinsed with three successive 10-mL aliquots of the extraction solvent and added to the separatory funnel. The ratio of solvent to aqueous sample should be maintained at 1:3. Extract the sample by vigorously shaking the separatory funnel for 5 min. After complete separation of the phases, remove the solvent and transfer to a Kuderna-Danish concentrator (K-D), filtering through a bed of precleaned, dry sodium sulfate. Repeat the extraction step two additional times. Adjust the pH to 11 with 6 N sodium hydroxide and reextract combining the acid and base extracts. Rinse the sodium sulfate into the K-D with fresh solvent and discard the desiccant. Add Teflon boiling chips and concentrate to 10 mL by reducing the volume to slightly less than 10 mL and then bringing to volume with fresh solvent. In order to achieve the necessary detection limit, the sample volume can be further reduced to 1 mL by using a micro column K-D or nitrogen blow-down. Should the sample start to exhibit precipitation, the concentration step should be stopped and the sample redissolved with fresh solvent taking the volume to some finite amount. After adding a standard (for the purpose of quantitation by GC/MS), the sample is ready for analysis, as discussed in Paragraph 8.2.

8.1.3 **Impinger:** Spike the sample with the surrogate standards; measure and record the volume and transfer to a separatory funnel. Proceed as described in Paragraph 8.1.2.

8.1.4 **XAD-2:** Spike the resin directly with the surrogate standards. Transfer the resin to the all-glass thimbles by the following procedure (care should be taken so as not to contaminate the thimble by touching it with anything other than tweezers or other solvent-rinsed mechanical holding devices). Suspend the XAD-2 module directly over the thimble. The glass frit of the module (see Figure 2) should be in the up position. The thimble is contained in a clean beaker, which will serve to catch the solvent rinses. Using a Teflon squeeze bottle, flush the XAD-2 into the thimble. Thoroughly rinse the glass module with solvent into the beaker containing the thimble. Add the XAD-2 glass-wool plug to the thimble. Cover the XAD-2 in the thimble with a precleaned glass-wool plug sufficient to prevent the resin from floating into the solvent reservoir of the extractor. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. If a question arises concerning the completeness of the extraction, a second extraction, without a spike, is advised. The thimble is placed in the extractor and the rinse solvent contained in the beaker is added to the solvent reservoir. Additional solvent is added to make the reservoir approximately two-thirds full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle 5-6 times per hr. Extract the resin for 16 hr. Transfer the solvent and three 10-mL rinses of the reservoir to a K-D and concentrate as described in Paragraph 8.1.2.

8.1.5 **Particulate filter (and cyclone catch):** If particulate loading is to be determined, weigh the filter (and cyclone catch, if applicable). The particulate filter (and cyclone catch, if applicable) is transferred to the glass thimble and extracted simultaneously with the XAD-2 resin.

8.1.6 **Train solvent rinses:** All train rinses (i.e., probe, impinger, filter housing) using the extraction solvent and methanol are returned to the laboratory as a single sample. If the rinses are contained in more than one container, the intended spike is divided equally among the containers proportioned from a single syringe volume. Transfer the rinse to a separatory funnel and add a sufficient amount of organic-free water so that the methylene chloride becomes immiscible and its volume no longer increases with the addition of more water. The extraction and concentration steps are then performed as described in Paragraph 8.1.2.

8.2 Sample analysis:

8.2.1 The primary analytical tool for the measurement of emissions from hazardous waste incinerators is GC/MS using fused-silica capillary GC columns, as described in Method 8270 in Chapter Four of this manual. Because of the nature of GC/MS instrumentation and the cost associated

with sample analysis, prescreening of the sample extracts by gas chromatography/flame ionization detection (GC/FID) or with electron capture (GC/ECD) is encouraged. Information regarding the complexity and concentration level of a sample prior to GC/MS analysis can be of enormous help. This information can be obtained by using either capillary columns or less expensive packed columns. However, the FID screen should be performed with a column similar to that used with the GC/MS. Keep in mind that GC/FID has a slightly lower detection limit than GC/MS and, therefore, that the concentration of the sample can be adjusted either up or down prior to analysis by GC/MS.

8.2.2 The mass spectrometer will be operated in a full scan (40-450) mode for most of the analyses. The range for which data are acquired in a GC/MS run will be sufficiently broad to encompass the major ions, as listed in Chapter Four, Method 8270, for each of the designated POHCs in an incinerator effluent analysis.

8.2.3 For most purposes, electron ionization (EI) spectra will be collected because a majority of the POHCs give reasonable EI spectra. Also, EI spectra are compatible with the NBS Library of Mass Spectra and other mass spectral references, which aid in the identification process for other components in the incinerator process streams.

8.2.4 To clarify some identifications, chemical ionization (CI) spectra using either positive ions or negative ions will be used to elucidate molecular-weight information and simplify the fragmentation patterns of some compounds. In no case, however, should CI spectra alone be used for compound identification. Refer to Chapter Four, Method 8270, for complete descriptions of GC conditions, MS conditions, and quantitative and quantitative identification.

9.0 CALIBRATION

9.1 Probe nozzle: Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make measurements at three separate places across the diameter and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

9.2 Pitot tube: The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of EPA Method 2, or assigned a nominal coefficient of 0.84 if it is not visibly nicked, dented, or corroded and if it meets design and intercomponent spacing specifications.

9.3 Metering system:

9.3.1 Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry-gas meter dial readings to correspond to the wet-test meter readings, calibration factors may be used to correct the gas meter dial readings mathematically to the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: Make a 10-min calibration run at 0.00057 m^3/min (0.02 cfm); at the end of the run, take the difference of the measured wet-test and dry-gas meter volumes and divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.02 cfm).

9.3.2 After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single intermediate orifice setting (based on the previous field test). The vacuum shall be set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet-test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5%, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

9.3.3 **Leak-check of metering system:** That portion of the sampling train from the pump to the orifice meter (see Figure 1) should be leak-checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 6): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13-18 cm (5-7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for 1 min. A loss of pressure on the manometer indicates a leak in the meter box. Leaks, if present, must be corrected.

NOTE: If the dry-gas-meter coefficient values obtained before and after a test series differ by >5%, either the test series shall be voided or calculations for test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

9.4 Probe heater: The probe-heating system shall be calibrated before its initial use in the field according to the procedure outlined in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

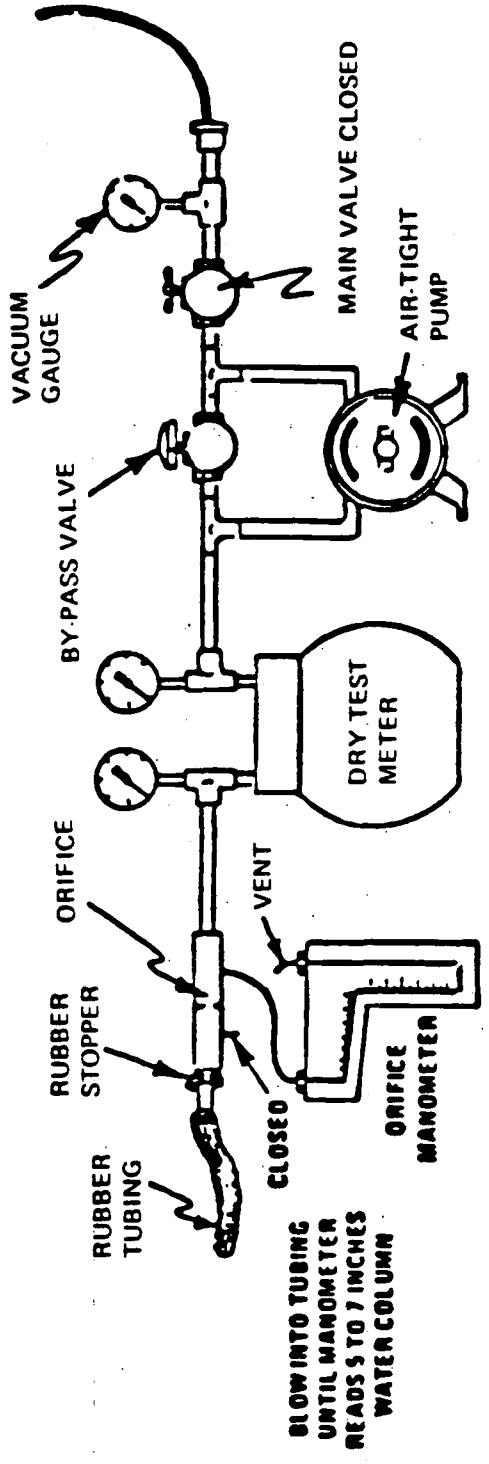

Figure 6. Leak-check of meter box.

9.5 Temperature gauges: Each thermocouple must be permanently and uniquely marked on the casting; all mercury-in-glass reference thermometers must conform to ASTM E-1 63C or 63F specifications. Thermocouples should be calibrated in the laboratory with and without the use of extension leads. If extension leads are used in the field, the thermocouple readings at ambient air temperatures, with and without the extension lead, must be noted and recorded. Correction is necessary if the use of an extension lead produces a change >1.5%.

9.5.1 **Impinger, organic module, and dry-gas meter thermocouples:** For the thermocouples used to measure the temperature of the gas leaving the impinger train and the XAD-2 resin bed, three-point calibration at ice-water, room-air, and boiling-water temperatures is necessary. Accept the thermocouples only if the readings at all three temperatures agree to ±2°C (3.6°F) with those of the absolute value of the reference thermometer.

9.5.2 **Probe and stack thermocouple:** For the thermocouples used to indicate the probe and stack temperatures, a three-point calibration at ice-water, boiling-water, and hot-oil-bath temperatures must be performed; it is recommended that room-air temperature be added, and that the thermometer and the thermocouple agree to within 1.5% at each of the calibration points. A calibration curve (equation) may be constructed (calculated) and the data extrapolated to cover the entire temperature range suggested by the manufacturer.

9.6 Barometer: Adjust the barometer initially and before each test series to agree to within ±25 mm Hg (0.1 in. Hg) of the mercury barometer or the corrected barometric pressure value reported by a nearby National Weather Service Station (same altitude above sea level).

9.7 Triple-beam balance: Calibrate the triple-beam balance before each test series, using Class-S standard weights; the weights must be within ±0.5% of the standards, or the balance must be adjusted to meet these limits.

10.0 CALCULATIONS

10.1 Carry out calculations. Round off figures after the final calculation to the correct number of significant figures.

10.2 Nomenclature:

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_d = Type S pitot tube coefficient (nominally 0.84 ± 0.02), dimensionless.

I = Percent of isokinetic sampling.

L_a = Maximum acceptable leakage rate for a leak-check, either pre-test or following a component change; equal to 0.00057 m^3/min (0.02 cfm) or 4% of the average sampling rate, whichever is less.

L_i = Individual leakage rate observed during the leak-check conducted prior to the "i^{th}" component change (i = 1, 2, 3...n) m^3/min (cfm).

L_p = Leakage rate observed during the post-test leak-check, m^3/min (cfm).

M_d = Stack-gas dry molecular weight, g/g-mole (lb/lb-mole).

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack-gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 mm Hg-m^3/K-g-mole (21.85 in. Hg-ft^3/°R-lb-mole).

T_m = Absolute average dry-gas meter temperature (see Figure 6), K (°R).

T_s = Absolute average stack-gas temperature (see Figure 6), K (°R).

T_{std} = Standard absolute temperature, 293K (528°R).

V_{lc} = Total volume of liquid collected in the organic module condensate knockout trap, the impingers, and silica gel, mL.

V_m = Volume of gas sample as measured by dry-gas meter, dscm (dscf).

$V_{m(std)}$ = Volume of gas sample measured by the dry-gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

V_s = Stack-gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/sec (ft/sec).

W_a = Weight of residue in acetone wash, mg.

γ = Dry-gas-meter calibration factor, dimensionless.

ΔH = Average pressure differential across the orifice meter (see Figure 2), mm H_2O (in. H_2O).

ρ_w = Density of water, 0.9982 g/mL (0.002201 lb/mL).

θ = Total sampling time, min.

θ_1 = Sampling time interval from the beginning of a run until the first component change, min.

θ_i = Sampling time interval between two successive component changes, beginning with the interval between the first and second changes, min.

θ_p = Sampling time interval from the final (n^{th}) component change until the end of the sampling run, min.

13.6 = Specific gravity of mercury.

60 = sec/min.

100 = Conversion to percent.

10.3 Average dry-gas-meter temperature and average orifice pressure drop: See data sheet (Figure 5, above).

10.4 Dry-gas volume: Correct the sample measured by the dry-gas meter to standard conditions (20°C, 760 mm Hg [68°F, 29.92 in. Hg]) by using Equation 1:

$$V_{m(std)} = V_m \gamma \frac{T_{std}}{T_m} \frac{P_{bar} + \Delta H/13.6}{P_{std}} = K_1 V_m \gamma \frac{P_{bar} + \Delta H/13.6}{T_m} \qquad (1)$$

where:

K_1 = 0.3858 K/mm Hg for metric units, or
K_1 = 17.64°R/in. Hg for English units.

It should be noted that Equation 1 can be used as written, unless the leakage rate observed during any of the mandatory leak-checks (i.e., the post-test leak-check or leak-checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, Equation 1 must be modified as follows:

a. Case I (no component changes made during sampling run): Replace V_m in Equation 1 with the expression:

$$V_m - (L_p - L_a)$$

b. Case II (one or more component changes made during the sampling run): Replace V_m in Equation 1 by the expression:

$$V_m - (L_1 - L_a)\theta_1 - \sum_{i=2}^{n} (L_i - L_a)\theta_1 - (L_p - L_a)\theta_p$$

and substitute only for those leakage rates (L_1 or L_p) that exceed L_a.

10.5 Volume of water vapor:

$$V_{w(std)} = V_{lc} \frac{P_w}{M_w} \frac{RT_{std}}{P_{std}} = K_2 V_{lc} \quad (2)$$

where:

K_2 = 0.001333 m^3/mL for metric units, or
K_2 = 0.04707 ft^3/mL for English units.

10.6 Moisture content:

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \quad (3)$$

NOTE: In saturated or water-droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 3) and a second from the assumption of saturated conditions. The lower of the two values of B_w shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the Note to Section 1.2 of Method 4. For the purposes of this method, the average stack-gas temperature from Figure 6 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ±1°C (2°F).

10.7 Conversion factors:

From	To	Multiply by
scf	m^3	0.02832
g/ft^3	gr/ft^3	15.43
g/ft^3	lb/ft^3	2.205×10^{-3}
g/ft^3	g/m^3	35.31

10.8 Isokinetic variation:

10.8.1 **Calculation from raw data:**

$$I = \frac{100\ T_s[K_3 F_{1c} + (V_m/T_m)\ (P_{bar} + \Delta H/13.6)]}{60\theta V_s P_s A_n} \qquad (4)$$

where:

K_3 = 0.003454 mm Hg-m^3/mL-K for metric units, or
K_3 = 0.002669 in. Hg-ft^3/mL-°R for English units.

10.8.2 **Calculation for intermediate values:**

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} V_s \theta A_n P_s 60(1-B_{ws})} \qquad (5)$$

$$= K_4 \frac{T_s V_{m(std)}}{P_s V_s A_n \theta (1-B_{ws})}$$

where:

K_4 = 4.320 for metric units, or
K_4 = 0.09450 for English units.

10.8.3 **Acceptable results:** If $90\% \leq I \leq 110\%$, the results are acceptable. If the results are low in comparison with the standard and I is beyond the acceptable range, or if I is less than 90%, the Administrator may opt to accept the results.

10.9 To determine the minimum sample volume that shall be collected, the following sequence of calculations shall be used.

10.9.1 From prior analysis of the waste feed, the concentration of POHCs introduced into the combustion system can be calculated. The degree of destruction and removal efficiency that is required is used to determine the maximum amount of POHC allowed to be present in the effluent. This may be expressed as:

$$\frac{(WF)\ (POHC_i\ conc)}{100} \quad \frac{(100-\%DRE)}{100} = \text{Max } POHC_i \text{ Mass} \qquad (6)$$

where:

WF = mass flow rate of waste feed per hr, g/hr (lb/hr).

$POHC_i$ = concentration of Principal Organic Hazardous Compound (wt %) introduced into the combustion process.

DRE = percent Destruction and Removal Efficiency required.

Max POHC = mass flow rate (g/hr [lb/hr]) of POHC emitted from the combustion source.

10.9.2 The average discharge concentration of the POHC in the effluent gas is determined by comparing the Max POHC with the volumetric flow rate being exhausted from the source. Volumetric flow rate data are available as a result of preliminary Method 1-4 determinations:

$$\frac{\text{Max POHC}_i \text{ Mass}}{DV_{eff(std)}} = \text{Max POHC}_i \text{ conc} \qquad (7)$$

where:

$DV_{eff(std)}$ = volumetric flow rate of exhaust gas, dscm (dscf).

$POHC_i$ conc = anticipated concentration of the POHC in the exhaust gas stream, g/dscm (lb/dscf).

10.9.3 In making this calculation, it is recommended that a safety margin of at least ten be included:

$$\frac{LDL_{POHC} \times 10}{POHC_i \text{ conc}} = V_{TBC} \qquad (8)$$

where:

LDL_{POHC} = detectable amount of POHC in entire sampling train.
NOTE: The whole extract from an XAD-2 cartridge is seldom if ever, injected at once. Therefore, if aliquoting factors are involved, the LDL_{POHC} is not the same as the analytical (or column) detection limit.

V_{TBC} = minimum dry standard volume to be collected at dry-gas meter.

10.10 Concentration of any given POHC in the gaseous emissions of a combustion process:

1) Multiply the concentration of the POHC as determined in Method 8270 by the final concentration volume, typically 10 mL.

C_{POHC} (ug/mL) x sample volume (mL) = amount (ug) of POHC in sample (9)

where:

C_{POHC} = concentration of POHC as analyzed by Method 8270.

2) Sum the amount of POHC found in all samples associated with a single train.

Total (ug) = XAD-2 (ug) + condensate (ug) + rinses (ug) + impinger (ug) (10)

3) Divide the total ug found by the volume of stack gas sampled (m^3).

(Total ug)/(train sample volume) = concentration of POHC (ug/m^3) (11)

11.0 QUALITY CONTROL

11.1 Sampling: See EPA Manual 600/4-77-027b for Method 5 quality control.

11.2 Analysis: The quality assurance program required for this study includes the analysis of field and method blanks, procedure validations, incorporation of stable labeled surrogate compounds, quantitation versus stable labeled internal standards, capillary column performance checks, and external performance tests. The surrogate spiking compounds selected for a particular analysis are used as primary indicators of the quality of the analytical data for a wide range of compounds and a variety of sample matrices. The assessment of combustion data, positive identification, and quantitation of the selected compounds are dependent on the integrity of the samples received and the precision and accuracy of the analytical methods employed. The quality assurance procedures for this method are designed to monitor the performance of the analytical method and to provide the required information to take corrective action if problems are observed in laboratory operations or in field sampling activities.

11.2.1 **Field Blanks:** Field blanks must be submitted with the samples collected at each sampling site. The field blanks include the sample bottles containing aliquots of sample recovery solvents, unused filters, and resin cartridges. At a minimum, one complete sampling train will be assembled in the field staging area, taken to the sampling area, and leak-checked at the beginning and end of the testing (or for the same total number of times as the actual test train). The filter housing and probe of the blank train will be heated during the sample test. The train will be recovered as if it were an actual test sample. No gaseous sample will be passed through the sampling train.

11.2.2 **Method blanks:** A method blank must be prepared for each set of analytical operations, to evaluate contamination and artifacts that can be derived from glassware, reagents, and sample handling in the laboratory.

11.2.3 Refer to Method 8270 for additional quality control considerations.

12.0 METHOD PERFORMANCE

12.1 Method performance evaluation: Evaluation of analytical procedures for a selected series of compounds must include the sample-preparation procedures and each associated analytical determination. The analytical procedures should be challenged by the test compounds spiked at appropriate levels and carried through the procedures.

12.2 Method detection limit: The overall method detection limits (lower and upper) must be determined on a compound-by-compound basis because different compounds may exhibit different collection, retention, and extraction efficiencies as well as instrumental minimum detection limit (MDL). The method detection limit must be quoted relative to a given sample volume. The upper limits for the method must be determined relative to compound retention volumes (breakthrough).

12.3 Method precision and bias: The overall method precision and bias must be determined on a compound-by-compound basis at a given concentration level. The method precision value would include a combined variability due to sampling, sample preparation, and instrumental analysis. The method bias would be dependent upon the collection, retention, and extraction efficiency of the train components. From evaluation studies to date using a dynamic spiking system, method biases of -13% and -16% have been determined for toluene and 1,1,2,2-tetrachloroethane, respectively. A precision of 19.9% was calculated from a field test data set representing seven degrees of freedom which resulted from a series of paired, unspiked Semivolatile Organic Sampling trains (Semi-VOST) sampling emissions from a hazardous waste incinerator.

13.0 REFERENCES

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METHOD 0010, APPENDIX A

PREPARATION OF XAD-2 SORBENT RESIN

1.0 SCOPE AND APPLICATION

1.1 XAD-2 resin as supplied by the manufacturer is impregnated with a bicarbonate solution to inhibit microbial growth during storage. Both the salt solution and any residual extractable monomer and polymer species must be removed before use. The resin is prepared by a series of water and organic extractions, followed by careful drying.

2.0 EXTRACTION

2.1 Method 1: The procedure may be carried out in a giant Soxhlet extractor. An all-glass thimble containing an extra-coarse frit is used for extraction of XAD-2. The frit is recessed 10-15 mm above a crenellated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass-wool plug and stainless steel screen because it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with Type II water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with H_2O for 8 hr.
Methyl alcohol	Extract for 22 hr.
Methylene chloride	Extract for 22 hr.
Methylene chloride (fresh)	Extract for 22 hr.

2.2 Method 2:

2.2.1 As an alternative to Soxhlet extraction, a continuous extractor has been fabricated for the extraction sequence. This extractor has been found to be acceptable. The particular canister used for the apparatus shown in Figure A-1 contains about 500 g of finished XAD-2. Any size may be constructed; the choice is dependent on the needs of the sampling programs. The XAD-2 is held under light spring tension between a pair of coarse and fine screens. Spacers under the bottom screen allow for even distribution of clean solvent. The three-necked flask should be of sufficient size (3-liter in this case) to hold solvent

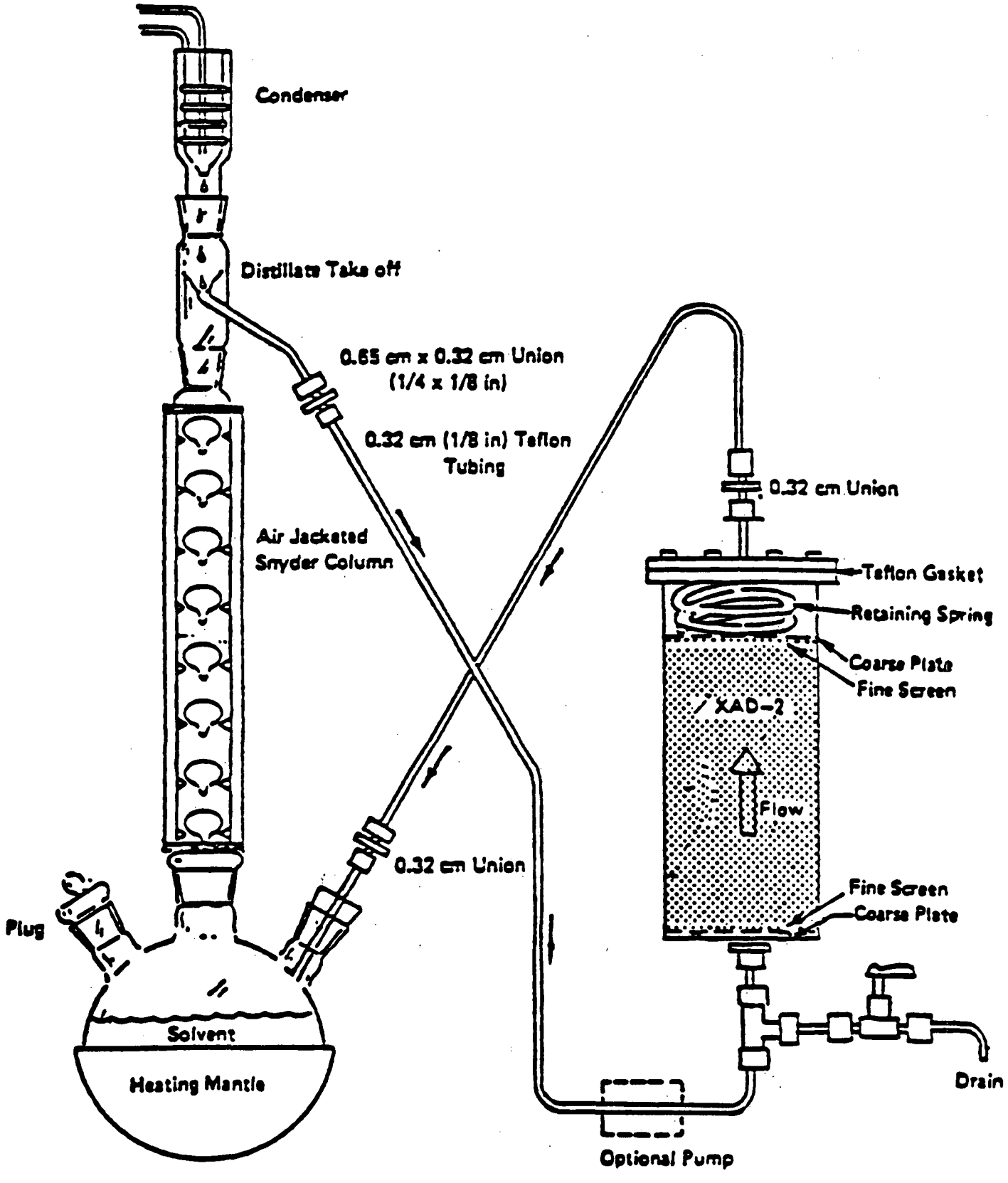


Figure A-1. XAD-2 cleanup extraction apparatus.

equal to twice the dead volume of the XAD-2 canister. Solvent is refluxed through the Snyder column, and the distillate is continuously cycled up through the XAD-2 for extraction and returned to the flask. The flow is maintained upward through the XAD-2 to allow maximum solvent contact and prevent channeling. A valve at the bottom of the canister allows removal of solvent from the canister between changes.

2.2.2 Experience has shown that it is very difficult to cycle sufficient water in this mode. Therefore the aqueous rinse is accomplished by simply flushing the canister with about 20 liters of distilled water. A small pump may be useful for pumping the water through the canister. The water extraction should be carried out at the rate of about 20-40 mL/min.

2.2.3 After draining the water, subsequent methyl alcohol and methylene chloride extractions are carried out using the refluxing apparatus. An overnight or 10- to 20-hr period is normally sufficient for each extraction.

2.2.4 All materials of construction are glass, Teflon, or stainless steel. Pumps, if used, should not contain extractable materials. Pumps are not used with methanol and methylene chloride.

3.0 DRYING

3.1 After evaluation of several methods of removing residual solvent, a fluidized-bed technique has proved to be the fastest and most reliable drying method.

3.2 A simple column with suitable retainers, as shown in Figure A-2, will serve as a satisfactory column. A 10.2-cm (4-in.) Pyrex pipe 0.6 m (2 ft) long will hold all of the XAD-2 from the extractor shown in Figure A-1 or the Soxhlet extractor, with sufficient space for fluidizing the bed while generating a minimum resin load at the exit of the column.

3.3 Method 1: The gas used to remove the solvent is the key to preserving the cleanliness of the XAD-2. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has routinely proved to be a reliable source of large volumes of gas free from organic contaminants. The liquid nitrogen cylinder is connected to the column by a length of precleaned 0.95-cm (3/8-in.) copper tubing, coiled to pass through a heat source. As nitrogen is bled from the cylinder, it is vaporized in the heat source and passes through the column. A convenient heat source is a water bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40°C. Experience has shown that about 500 g of XAD-2 may be dried overnight by consuming a full 160-liter cylinder of liquid nitrogen.

3.4 Method 2: As a second choice, high-purity tank nitrogen may be used to dry the XAD-2. The high-purity nitrogen must first be passed through a bed

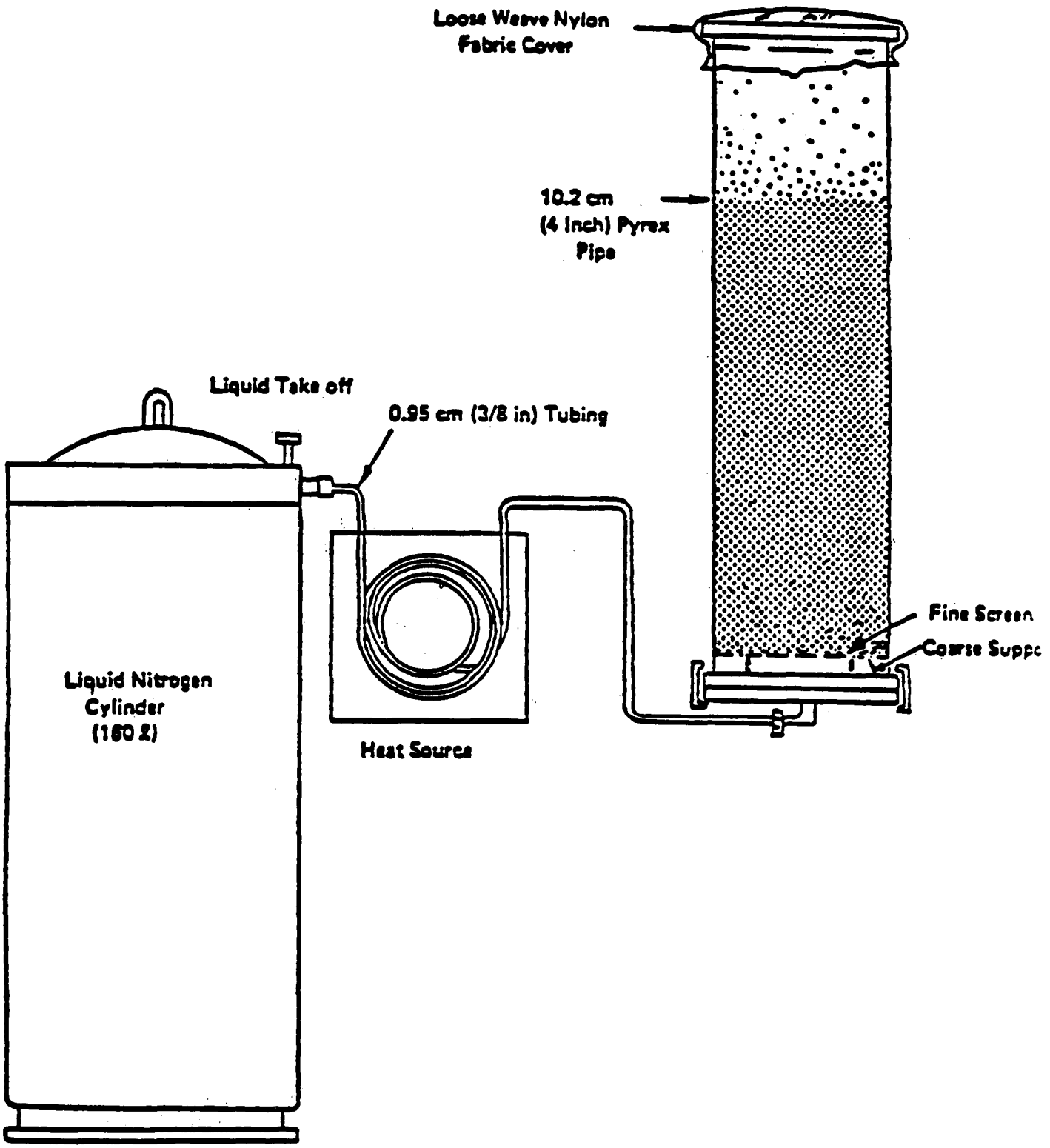


Figure A-2. XAD-2 fluidized-bed drying apparatus.

of activated charcoal approximately 150 mL in volume. With either type of drying method, the rate of flow should gently agitate the bed. Excessive fluidization may cause the particles to break up.

4.0 QUALITY CONTROL PROCEDURES

4.1 For both Methods 1 and 2, the quality control results must be reported for the batch. The batch must be reextracted if the residual extractable organics are >20 ug/mL by TCO analysis or the gravimetric residue is >0.5 mg/20 g XAD-2 extracted. (See also section 5.1, Method 0010.)

4.2 Four control procedures are used with the final XAD-2 to check for (1) residual methylene chloride, (2) extractable organics (TCO), (3) specific compounds of interest as determined by GC/MS, as described in Section 4.5 below, and (4) residue (GRAV).

4.3 Procedure for residual methylene chloride:

4.3.1 **Description:** A 1±0.1-g sample of dried resin is weighed into a small vial, 3 mL of toluene are added, and the vial is capped and well shaken. Five uL of toluene (now containing extracted methylene chloride) are injected into a gas chromatograph, and the resulting integrated area is compared with a reference standard. The reference solution consists of 2.5 uL of methylene chloride in 100 mL of toluene, simulating 100 ug of residual methylene chloride on the resin. The acceptable maximum content is 1,000 ug/g resin.

4.3.2 **Experimental:** The gas chromatograph conditions are as follows:

6-ft x 1/8-in. stainless steel column containing 10% OV-101 on 100/120 Supelcoport;

Helium carrier at 30 mL/min;

FID operated on 4 x 10^{-11} A/mV;

Injection port temperature: 250°C;

Detector temperature: 305°C;

Program: 30°C(4 min) 40°C/min 250°C (hold); and

Program terminated at 1,000 sec.

4.4 Procedure for residual extractable organics:

4.4.1 **Description:** A 20±0.1-g sample of cleaned, dried resin is weighed into a precleaned alundum or cellulose thimble which is plugged with cleaned glass wool. (Note that 20 g of resin will fill a thimble, and the

resin will float out unless well plugged.) The thimble containing the resin is extracted for 24 hr with 200-mL of pesticide- grade methylene chloride (Burdick and Jackson pesticide-grade or equivalent purity). The 200-mL extract is reduced in volume to 10-mL using a Kuderna-Danish concentrator and/or a nitrogen evaporation stream. Five uL of that solution are analyzed by gas chromatography using the TCO analysis procedure. The concentrated solution should not contain >20 ug/mL of TCO extracted from the XAD-2. This is equivalent to 10 ug/g of TCO in the XAD-2 and would correspond to 1.3 mg of TCO in the extract of the 130-g XAD-2 module. Care should be taken to correct the TCO data for a solvent blank prepared (200 mL reduced to 10 mL) in a similar manner.

4.4.2 **Experimental:** Use the TCO analysis conditions described in the revised Level 1 manual (EPA 600/7-78-201).

4.5 GC/MS Screen: The extract, as prepared in paragraph 4.4.1, is subjected to GC/MS analysis for each of the individual compounds of interest. The GC/MS procedure is described in Chapter Four, Method 8270. The extract is screened at the MDL of each compound. The presence of any compound at a concentration >25 ug/mL in the concentrated extract will require the XAD-2 to be recleaned by repeating the methylene chloride step.

4.6 Methodology for residual gravimetric determination: After the TCO value and GC/MS data are obtained for the resin batch by the above procedures, dry the remainder of the extract in a tared vessel. There must be <0.5 mg residue registered or the batch of resin will have to be extracted with fresh methylene chloride again until it meets this criterion. This level corresponds to 25 ug/g in the XAD-2, or about 3.25 mg in a resin charge of 130 g.

METHOD 0010, APPENDIX B

TOTAL CHROMATOGRAPHABLE ORGANIC MATERIAL ANALYSIS

1.0 SCOPE AND APPLICATION

1.1 In this procedure, gas chromatography is used to determine the quantity of lower boiling hydrocarbons (boiling points between 90° and 300°C) in the concentrates of all organic solvent rinses, XAD-2 resin and LC fractions - when Method 1 is used (see References, Method 0010) - encountered in Level 1 environmental sample analyses. Data obtained using this procedure serve a twofold purpose. First, the total quantity of the lower boiling hydrocarbons in the sample is determined. Then whenever the hydrocarbon concentrations in the original concentrates exceed 75 ug/m^3, the chromatography results are reexamined to determine the amounts of individual species.

The extent of compound identification is limited to representing all materials as normal alkanes based upon comparison of boiling points. Thus the method is not qualitative. In a similar manner, the analysis is semiquantitative; calibrations are prepared using only one hydrocarbon. They are replicated but samples routinely are not.

1.2 Application: This procedure applies solely to the Level 1 C7-C16 gas chromatographic analysis of concentrates of organic extracts, neat liquids, and of LC fractions. Throughout the procedure, it is assumed the analyst has been given a properly prepared sample.

1.3 Sensitivity: The sensitivity of this procedure, defined as the slope of a plot of response versus concentration, is dependent on the instrument and must be verified regularly. TRW experience indicates the nominal range is of the order of 77 uV·V·sec·uL/ng of n-heptane and 79 uV·sec·ul/ng of n-hexadecane. The instrument is capable of perhaps one hundredfold greater sensitivity. The level specified here is sufficient for Level 1 analysis.

1.4 Detection limit: The detection limit of this procedure as written is 1.3 ng/uL for a 1 uL injection of n-decane. This limit is arbitrarily based on defining the minimum detectable response as 100 uv·sec. This is an easier operational definition than defining the minimum detection limit to be that amount of material which yields a signal twice the noise level.

1.5 Range: The range of the procedure will be concentrations of 1.3 ng/uL and greater.

1.6 Limitations

1.6.1 Reporting limitations: It should be noted that a typical environmental sample will contain compounds which: (a) will not elute in the specified boiling ranges and thus will not be reported, and/or (b)

will not elute from the column at all and thus will not be reported. Consequently, the organic content of the sample as reported is a lower bound and should be regarded as such.

1.6.2 **Calibration limitations:** Quantitation is based on calibration with n-decane. Data should therefore be reported as, e.g., mg C8/m^3 as n-decane. Since response varies linearly with carbon number (over a wide range the assumption may involve a 20% error), it is clear that heptane (C7) detected in a sample and quantitated as decane will be overestimated. Likewise, hexadecane (C16) quantitated as decane will be underestimated. From previous data, it is estimated the error involved is on the order of 6-7%.

1.6.3 **Detection limitations:** The sensitivity of the flame ionization detector varies from compound to compound. However, n-alkanes have a greater response than other classes. Consequently, using an n-alkane as a calibrant and assuming equal responses of all other compounds tends to give low reported values.

2.0 SUMMARY OF METHOD

2.1 A mL aliquot of all 10-mL concentrates is disbursed for GC-TCO analysis. With boiling point-retention time and response-amount calibration curves, the data (peak retention times and peak areas) are interpreted by first summing peak areas in the ranges obtained from the boiling point-retention time calibration. Then, with the response-amount calibration curve, the area sums are converted to amounts of material in the reported boiling point ranges.

2.2 After the instrument is set up, the boiling point-retention time calibration is effected by injecting a mixture of n-C7 through n-C16 hydrocarbons and operating the standard temperature program. Response-quantity calibrations are accomplished by injecting n-decane in n-pentane standards and performing the standard temperature program.

2.3 Definitions

2.3.1 **GC:** Gas chromatography or gas chromatograph.

2.3.2 **C7-C16 n-alkanes:** Heptane through hexadecane.

2.3.3 **GCA temperature program:** 4 min isothermal at 60°C, 10°C/min from 60° to 220°C.

2.3.4 **TRW temperature program:** 5 min isothermal at room temperature, then program from 30°C to 250°C at 15°C/min.

3.0 INTERFERENCES

Not applicable.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: This procedure is intended for use on a Varian 1860 gas chromatograph, equipped with dual flame ionization detectors and a linear temperature programmer. Any equivalent instrument can be used provided that electrometer settings, etc., be changed appropriately.

4.2 Gases:

4.2.1 **Helium:** Minimum quality is reactor grade. A 4A or 13X molecular sieve drying tube is required. A filter must be placed between the trap and the instrument. The trap should be recharged after every third tank of helium.

4.2.2 **Air:** Zero grade is satisfactory.

4.2.3 **Hydrogen:** Zero grade.

4.3 Syringe: Syringes are Hamilton 701N, 10 uL, or equivalent.

4.4 Septa: Septa will be of such quality as to produce very low bleed during the temperature program. An appropriate septum is Supelco Microsep 138, which is Teflon-backed. If septum bleed cannot be reduced to a negligible level, it will be necessary to install septum swingers on the instrument.

4.5 Recorder: The recorder of this procedure must be capable of not less than 1 mV full-scale display, a 1-sec time constant and 0.5 in. per min chart rate.

4.6 Integrator: An integrator is required. Peak area measurement by hand is satisfactory but too time-consuming. If manual integration is required, the method of "height times width at half height" is used.

4.7 Columns:

4.7.1 **Preferred column:** 6 ft x 1/8 in. O.D. stainless steel column of 10% OV-101 on 100/120 mesh Supelcoport.

4.7.2 **Alternate column:** 6 ft x 1/8 in. O.D. stainless steel column of 10% OV-1 (or other silicon phase) on 100/120 mesh Supelcoport.

4.8 Syringe cleaner: Hamilton syringe cleaner or equivalent connected to a suitable vacuum source.

5.0 REAGENTS

5.1 Pentane: "Distilled-in-Glass" (reg. trademark) or "Nanograde" (reg. trademark) for standards and for syringe cleaning.

5.2 Methylene chloride: "Distilled-in-Glass" (reg. trademark) or "Nanograde" (reg. trademark) for syringe cleaning.

6.0 SAMPLING HANDLING AND PRESERVATION

6.1 The extracts are concentrated in a Kuderna-Danish evaporator to a volume less than 10 mL. The concentrate is then quantitatively transferred to a 10-mL volumetric flask and diluted to volume. A 1-mL aliquot is taken for both this analysis and possible subsequent GC/MS analysis and set aside in the sample bank. For each GC-TCO analysis, obtain the sample sufficiently in advance to allow it to warm to room temperature. For example, after one analysis is started, return that sample to the sample bank and take the next sample.

7.0 PROCEDURES

7.1 Setup and checkout: Each day, the operator will verify the following:

7.1.1 That supplies of carrier gas, air and hydrogen are sufficient, i.e., that each tank contains > 100 psig.

7.1.2 That, after replacement of any gas cylinder, all connections leading to the chromatograph have been leak-checked.

7.1.3 That the carrier gas flow rate is 30 ± 2 mL/min, the hydrogen flow rate is 30 ± 2 mL/min, and the air flow rate is 300 ± 20 mL/min.

7.1.4 That the electrometer is functioning properly.

7.1.5 That the recorder and integrator are functioning properly.

7.1.6 That the septa have been leak-checked (leak-checking is effected by placing the soap bubble flow meter inlet tube over the injection port adaptors), and that no septum will be used for more than 20 injections.

7.1.7 That the list of samples to be run is ready.

7.2 Retention time calibration:

7.2.1 To obtain the temperature ranges for reporting the results of the analyses, the chromatograph is given a normal boiling point-retention time calibration. The n-alkanes, their boiling points, and data reporting ranges are given in the table below:

	NBP,°C	Reporting Range,°C	Report As
n-heptane	98	90-110	C7
n-octane	126	110-140	C8
n-nonane	151	140-160	C9
n-decane	174	160-180	C10
n-undecane	194	180-200	C11
n-dodecane	214	200-220	C12
n-tridecane	234	220-240	C13
n-tetradecane	252	240-260	C14
n-pentadecane	270	260-280	C15
n-hexadecane	288	280-300	C16

7.2.2 **Preparation of standards:** Preparing a mixture of the C7-C16 alkanes is required. There are two approaches: (1) use of a standards kit (e.g., Polyscience Kit) containing bottles of mixtures of selected n-alkanes which may be combined to produce a C7-C16 standard; or (2) use of bottles of the individual C7-C16 alkanes from which accurately known volumes may be taken and combined to give a C7-C16 mixture.

7.2.3 **Procedure for retention time calibration:** This calibration is performed at the start of an analytical program; the mixture is chromatographed at the start of each day. To attain the required retention time precision, both the carrier gas flow rate and the temperature program specifications must be observed. Details of the procedure depend on the instrument being used. The general procedure is as follows:

7.2.3.1 Set the programmer upper limit at 250°C. If this setting does not produce a column temperature of 250°C, find the correct setting.

7.2.3.2 Set the programmer lower limit at 30°C.

7.2.3.3 Verify that the instrument and samples are at room temperature.

7.2.3.4 Inject 1 uL of the n-alkane mixture.

7.2.3.5 Start the integrator and recorder.

7.2.3.6 Allow the instrument to run isothermally at room temperature for five min.

7.2.3.7 Shut the oven door.

7.2.3.8 Change the mode to Automatic and start the temperature program.

7.2.3.9 Repeat Steps 1-9 a sufficient number of times so that the relative standard deviation of the retention times for each peak is <5%.

7.3 Response calibration:

7.3.1 For the purposes of a Level 1 analysis, response-quantity calibration with n-decane is adequate. A 10-uL volume of n-decane is injected into a tared 10 mL volumetric flask. The weight injected is obtained and the flask is diluted to the mark with n-pentane. This standard contains about 730 ng n-decane per uL n-pentane. The exact concentration depends on temperature, so that a weight is required. Two serial tenfold dilutions are made from this standard, giving standards at about 730, 73, and 7.3 ng n-decane per uL n-pentane, respectively.

7.3.2 **Procedure for response calibration:** This calibration is performed at the start of an analytical program and monthly thereafter. The most concentrated standard is injected once each day. Any change in calibration necessitates a full calibration with new standards. Standards are stored in the refrigerator locker and are made up monthly.

7.3.2.1 Verify that the instrument is set up properly.

7.3.2.2 Set electrometer at 1×10^{-10} A/mV.

7.3.2.3 Inject 1 uL of the highest concentration standard.

7.3.2.4 Run standard temperature program as specified above.

7.3.2.5 Clean syringe.

7.3.2.6 Make repeated injections of all three standards until the relative standard deviations of the areas of each standard are ≤5%.

7.4 Sample analysis procedure:

7.4.1 The following apparatus is required:

7.4.1.1 **Gas chromatograph** set up and working.

7.4.1.2 **Recorder, integrator** working.

7.4.1.3 **Syringe and syringe cleaning apparatus.**

7.4.1.4 **Parameters:** Electrometer setting is 1×10^{-10} A/mV; recorder is set at 0.5 in./min and 1 mV full-scale.

7.4.2 Steps in the procedure are:

7.4.2.1 Label chromatogram with the data, sample number, etc.

7.4.2.2 Inject sample.

7.4.2.3 Start integrator and recorder.

7.4.2.4 After isothermal operation for 5 min, begin temperature program.

7.4.2.5 Clean syringe.

7.4.2.6 Return sample; obtain new sample.

7.4.2.7 When analysis is finished, allow instrument to cool. Turn chromatogram and integrator output and data sheet over to data analyst.

7.5 Syringe cleaning procedure:

7.5.1 Remove plunger from syringe.

7.5.2 Insert syringe into cleaner; turn on aspirator.

7.5.3 Fill pipet with pentane; run pentane through syringe.

7.5.4 Repeat with methylene chloride from a separate pipet.

7.5.5 Flush plunger with pentane followed by methylene chloride.

7.5.6 Repeat with methylene chloride.

7.6 Sample analysis decision criterion: The data from the TCO analyses of organic extract and rinse concentrates are first used to calculate the total concentration of C7-C16 hydrocarbon-equivalents (Paragraph 7.7.3) in the sample with respect to the volume of air actually sampled, i.e., ug/m^3. On this basis, a decision is made both on whether to calculate the quantity of each n-alkane equivalent present and on which analytical procedural pathway will be followed. If the total organic content is great enough to warrant continuing the analysis -- >500 ug/m^3 -- a TCO of less than 75 ug/m^3 will require only LC fractionation and gravimetric determinations and IR spectra to be obtained on each fraction. If the TCO is greater than 75 ug/m^3, then the first seven LC fractions of each sample will be reanalyzed using this same gas chromatographic technique.

7.7 Calculations:

7.7.1 **Boiling Point - Retention Time Calibration:** The required data for this calibration are on the chromatogram and on the data sheet. The data reduction is performed as follows:

7.7.1.1 Average the retention times and calculate relative standard deviations for each n-hydrocarbon.

7.7.1.2 Plot average retention times as abscissae versus normal boiling points as ordinates.

7.7.1.3 Draw in calibration curve.

7.7.1.4 Locate and record retention times corresonding to boiling ranges 90-100, 110-140, 140-160, 160-180, 180-200, 200-220, 220-240, 240-260, 260-280, 280-300°C.

7.7.2 **Response-amount calibration:** The required data for this calibration are on the chromatogram and on the data sheet. The data reduction is performed as follows:

7.7.2.1 Average the area responses of each standard and calculate relative standard deviations.

7.7.2.2 Plot response (uv·sec) as ordinate versus ng/uL as abscissa.

7.7.2.3 Draw in the curve. Perform least squares regression and obtain slope (uV·sec·uL/ng).

7.7.3 **Total C7-C16 hydrocarbons analysis:** The required data for this calculation are on the chromatogram and on the data sheet. The data reduction is performed as follows:

7.7.3.1 Sum the areas of all peaks within the retention time range of interest.

7.7.3.2 Convert this area (uV·sec) to ng/uL by dividing by the weight response for n-decane (uV·sec.uL/ng).

7.7.3.3 Multiply this weight by the total concentrate volume (10 mL) to get the weight of the C7-C16 hydrocarbons in the sample.

7.7.3.4 Using the volume of gas sampled or the total weight of sample acquired, convert the result of Step 7.7.3.3 above to ug/m^3.

7.7.3.5 If the value of total C7-C16 hydrocarbons from Step 7.7.3.4 above exceeds 75 ug/m^3, calculate individual hydrocarbon concentrations in accordance with the instructions in Paragraph 7.7.5.5 below.

7.7.4 **Individual C7-C16 n-Alkane Equivalent Analysis:** The required data from the analyses are on the chromatogram and on the data sheet. The data reduction is performed as follows:

7.7.4.1 Sum the areas of peaks in the proper retention time ranges.

7.7.4.2 Convert areas (uV·sec) to ng/uL by dividing by the proper weight response (uV·sec·uL/ng).

7.7.4.3 Multiply each weight by total concentrate volume (10 mL) to get weight of species in each range of the sample.

7.7.4.4 Using the volume of gas sampled on the total weight of sample acquired, convert the result of Step 7.7.4.3 above to ug/m^3.

8.0 QUALITY CONTROL

8.1 Appropriate QC is found in the pertinent procedures throughout the method.

9.0 METHOD PERFORMANCE

9.1 Even relatively comprehensive error propagation analysis is beyond the scope of this procedure. With reasonable care, peak area reproducibility of a standard should be of the order of 1% RSD. The relative standard deviation of the sum of all peaks in a fairly complex waste might be of the order of 5-10%. Accuracy is more difficult to assess. With good analytical technique, accuracy and precision should be of the order of 10-20%.

10.0 REFERENCES

1. Emissions Assessment of Conventional Stationary Combustion Systems: Methods and Procedure Manual for Sampling and Analysis, Interagency Energy/Environmental R&D Program, Industrial Environmental Research Laboratory, Research Triangle Park, NC 27711, EPA-600/7-79-029a, January 1979.

METHOD 0020

SOURCE ASSESSMENT SAMPLING SYSTEM (SASS)

1.0 PRINCIPLE AND APPLICATION

1.1 Principle

1.1.1 Particulate and semivolatile organic materials are withdrawn from a source at a constant rate near isokinetic conditions and are collected in a multicomponent sampling train.

1.1.2 Three heated cyclones and a heated high-efficiency fiber filter remove and collect the particulate material from the sample and a packed bed of porous polymeric resin adsorbs the condensible organic vapors.

1.1.3 Chemical analyses of the sample are conducted to determine the concentration and identity of the semivolatile organic species and gravimetric determinations are performed to approximate particulate emissions.

1.2 Application: This method is applicable to the preparation of semiquantitative estimates (within a factor of three) of the amounts and types of semivolatile organic and particulate materials that are discharged from incineration systems.

2.0 APPARATUS

2.1 Sampling Train: A schematic of the sampling train used in this method is given in Figure 1. This sampling train configuration is that of the Source Assessment Sampling System (SASS), as supplied by the manufacturer. Basic operating and maintenance procedures are described in the "Operating and Service Manual: Source Assessment Sampling System" supplied on purchase of the sampling system (Blake, 1977). Users should refer to this document and adopt, but not limit themselves to, its operating and maintenance procedures. The SASS train components and specifications are detailed below.

2.1.1 **Probe nozzles:** The probe nozzles are constructed of Type 316 seamless stainless steel tubing and have sharp leading edges. The nozzles are a hybrid elbow/buttonhook design, obtainable in diameters ranging from 0.31 to 1.91 cm (1/8 to 3/4 in.), and are interchangeable. Each nozzle should be calibrated according to the procedure outlined in Paragraph 7.2 of this method.

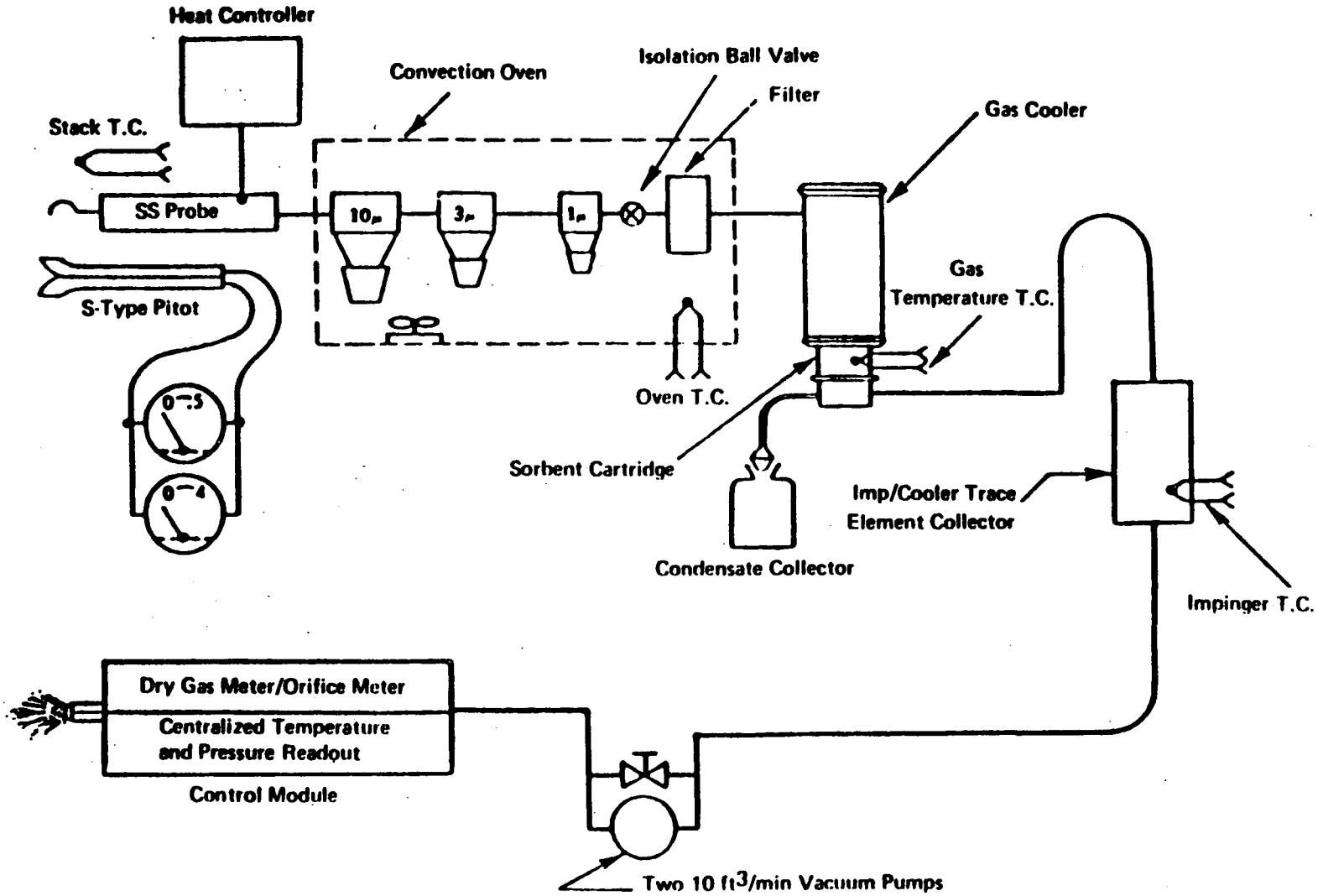


Figure 1. SASS Schematic Diagram.

2.1.2 **Probe Liner:**

2.1.2.1 The probe liner is also constructed of Type 316 seamless stainless steel tubing; attached to the liner is a proportional temperature controller capable of maintaining the liner surface temperature at 204 ± 20°C (400 ± 36°F) during sampling. The use of the proportional controller to control the liner surface temperature at the control module is preferred because the oven often cannot be reached for adjustment during sampling.

2.1.2.2 It should be noted that the measurement of the probe liner surface temperature is not an accurate measurement of the internal gas stream temperature, which is the temperature of interest. This source of error is caused by the temperature gradient that exists between the inner and outer walls of the liner. Monitoring of the actual gas stream temperature is impractical with the SASS trains as presently constructed. It is suggested that a one-time calibration be conducted in which the internal gas stream temperature is compared to the liner surface at various temperatures and at the standard SASS flow rate of 4.0 scfm.

2.1.2.3 The probe and probe liner can withstand points up to 370°C (700°F), at which temperature they will soften. However, stack temperatures greater than 288°C (550°F) may result in gas temperatures at the 10-um cyclone inlet greater than the recommended 204°C (400°F) and hence require the use of a special water- or forced-air-cooled probe.

2.1.3 **Pitot tubes:** The pitot tubes are Type S, designed to meet the specifications of EPA Method 2 (see Reference below); these are attached to the probe sheath to allow constant monitoring of the stack gas velocity. The point of attachment to the sheath is such that the impact (high pressure) opening plane of the pitots is level with or above the sampling nozzle entry plane, as required by Method 2, to eliminate nozzle interference in velocity measurements. If calibration is not required, the pitot tubes are assigned a nominal coefficient of 0.84, as described in the calibration section of this method.

2.1.4 **Differential pressure gauges:** Three Magnehelic-type gauges are used. One gauge (0 to 0.5 in. H_2O) monitors the pressure drop across the orifice meter (ΔH_i); the other two gauges (0 to 0.5 and 0 to 4.0 in. H_2O) are connected in parallel and indicate the pressure differential across the pitot tubes used for measuring stack gas velocity.

2.1.5 **Filter holder and filter support:** The filter holder and filter support screen are constructed of Type 316 stainless steel with a

Teflon gasket providing an airtight seal around the circumference. The holder is attached immediately to the outlet of the 1-um cyclone or the cyclone bypass.

2.1.6 **Cyclone/Filter heating system:** The cyclone/filter heating system is an insulated double-walled oven, capable of maintaining the temperature in the area of the cyclones and filter holder around the recommended 204°C (400°F). A chromel-alumel thermocouple for temperature sensing allows feedback control of the temperature to within approximately 10%.

2.1.7 **Cyclone train:** The cyclone train consists of three cyclone separators in series, having nominal particle-size cutoff diameters of 10, 3, and 1 um respectively. The material of construction is Type 316 stainless steel with Teflon gaskets sealing the hoods and collector cups. The compact design of the 10-um cyclone is achieved by incorporating flow-interrupting vanes in the collection cup.

2.1.8 **Organic module:** The organic module consists of a thin-film heat exchanger/gas cooler, a sorbent cartridge, and a condensate collection trap. The temperature of the heat exchanger fluid is regulated by activating an immersion heater or routing the coolant through another heat exchanger in the impinger ice water bath. Water from the impinger bath is continually circulated through the inner reservoir of the gas cooler for additional cooling capacity. The sorbent cartridge encloses the polymeric adsorbent bed in a cylinder covered on both ends by 80-mesh, Type 316 stainless steel wire cloth. The cartridge holds approximately 150 grams of XAD-2 adsorbent resin. Condensed moisture from the gas stream is collected in a reservoir located directly beneath the packed sorbent bed. The drain valve of the reservoir should be coupled with a Teflon line to an appropriately sized (1- to 5-liter) glass storage container, as the capacity of the reservoir will typically be exceeded during a run.

2.1.9 **Impinger train:** The four impingers have a capacity of approximately 3 liters each and are constructed of pyrex glass. The caps are Teflon with stainless steel fittings and the impingers are interconnected by flexible Teflon or stainless steel tubing. The first two impingers are equipped with splash guards to minimize fluid carryover and the last impinger with a thermocouple mounted in the cap for monitoring the impinger train exit gas temperature.

2.1.10 **Pump/Metering system:** Two leak-free vane-type vacuum pumps connected in parallel are used to maintain the 4.0-scfm flow in the sampling system. Vacuum and differential pressure gauges, thermocouples capable of measuring temperature to within 3°C (5.4°F) and a dry gas meter capable of measuring volume to within 2% are supplied as the other necessary components for maintaining isokinetic sampling rates.

2.1.11 **Barometer:** An aneroid barometer, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.5 in. Hg), is required, unless the barometric reading is obtained from a nearby National Weather Station; the station value (i.e., the absolute barometric pressure) must be corrected for elevation differences between the weather station and the sampling point. The corrected value should reflect a decrease of 2.5 mm Hg (0.1 in. Hg) per 30-m (100-ft) elevation increase, and vice versa for elevation decrease. (See Paragraph 7.7).

2.1.12 **Gas density determination apparatus:** The length of a SASS run is typically sufficient to determine the average gas stream density during the run. EPA Method 3 should be consulted for detailed specifications for an integrated fixed gas sampling system. Analysis of the collected samples should be performed with an ORSAT analyzer or a GC/TCD system outfitted specifically for this purpose.

2.1.13 **Calibration/Field preparation log:** For documentation of calibration and preparation procedures, a permanently bound laboratory notebook is recommended, in which carbon copies are made of the data as they are being recorded. The carbon copies should be detachable and used only for separate storage in the test program archives.

2.2 Sample recovery:

2.2.1 **Probe liner brush:** The brush must have nylon bristles, a stainless steel wire handle, and extensions of stainless steel, Teflon, or other inert material. The combined extensions must be equal to or greater than the length of the probe.

2.2.2 **Probe nozzle brush:** The brush must have nylon bristles and a stainless steel wire handle, and be properly sized and shaped for cleaning the inner surfaces of the nozzle.

2.2.3 **Cyclone and filter holder brushes:** The brushes must have nylon bristles and a stainless steel wire handle, and be properly sized for cleaning the inner walls of these components. It is strongly recommended that a separate brush be used for sample recovery from each of these components to avoid cross contamination of one particle size fraction by another.

2.2.4 **Wash bottles:** Three are needed. Teflon or glass is required to avoid contamination of organic solvents; Teflon is preferred because it is unbreakable.

2.2.5 **Glass sample storage containers:** The containers must be chemically resistant, borosilicate glass bottles, 500-mL or 1,000-mL. Screw-cap liners should be Teflon or constructed so as to be leak-free and resistant to chemical attack by organic recovery solvents (narrow-mouth glass bottles have been found to exhibit less tendency toward leakage).

2.2.6 **Petri dishes:** These must be glass and sealed around the circumference with Teflon tape for storage and transport of filter samples.

2.2.7 **Graduated cylinder and triple-beam balance:** to measure condensed water to the nearest 1 mL or 0.5 g. Graduated cylinders must have subdivisions no greater than 2 mL. Equipment made of glass must be used for measuring the volume of any solution that will be subject to organic analysis. Laboratory triple-beam balances must be capable of weighing to $\pm$0.5 g or better.

2.2.8 **High-density linear polyethylene (HDLP) storage containers:** These are used for storage of the impingers.

2.2.9 **Plastic storage containers:** Airtight containers are necessary for storage of silica gel.

2.2.10 **Funnels:** Glass funnels must be used in recovering samples for organic analysis. Glass or plastic funnels may be used in other processes but care must be taken to segregate the two types.

3.0 REAGENTS AND MATERIALS

3.1 Filters: Glass fiber filters, 15.24 cm (6.0 in.) in diameter without organic binder, exhibiting 99.95% efficiency (<0.05% penetration) on 0.3-micron dioctyl phthalate smoke particles, conforming to the specifications outlined in ASTM Standard Method D2986-71. Test data from the supplier's quality control program are sufficient for this purpose. The filter material must also be unreactive to SO_2 and SO_3.

3.2 Adsorbent resin: Porous polymeric resin, XAD-2, is used. The resin must be cleaned prior to use. The resin must not exhibit a blank higher than 4 mg/kg of total chromatographable organics (TCO) prior to use. Once cleaned, the resin should be stored in a wide-mouth amber glass container and the headspace purged with nitrogen to limit exposure to ambient air. Resin should be used within 2 wk of preparation.

3.3 Silica gel: Indicating type, 6 to 16 mesh. If previously used, dry at 175°C (350°F) for 2 hr. New silica gel may be used as received.

3.4 Impinger solutions: Since the impinger solutions are typically used for the determination of gas-stream water-vapor content, Type II water should be used. If specific inorganic species are to be determined (e.g., hydrochloric acid when burning chlorinated organic material), then other appropriate collecting solutions (in the above example, dilute base) must be used.

3.5 Crushed ice: Commercially available. Quantities ranging from 50 to 100 lb may be necessary during a run, depending upon ambient air temperatures.

3.6 Methanol/Methylene chloride: Distilled-in-glass or pesticide-grade methanol and methylene chloride are required.

4.0 SAMPLING PROCEDURE

4.1 Sampling equipment calibration:

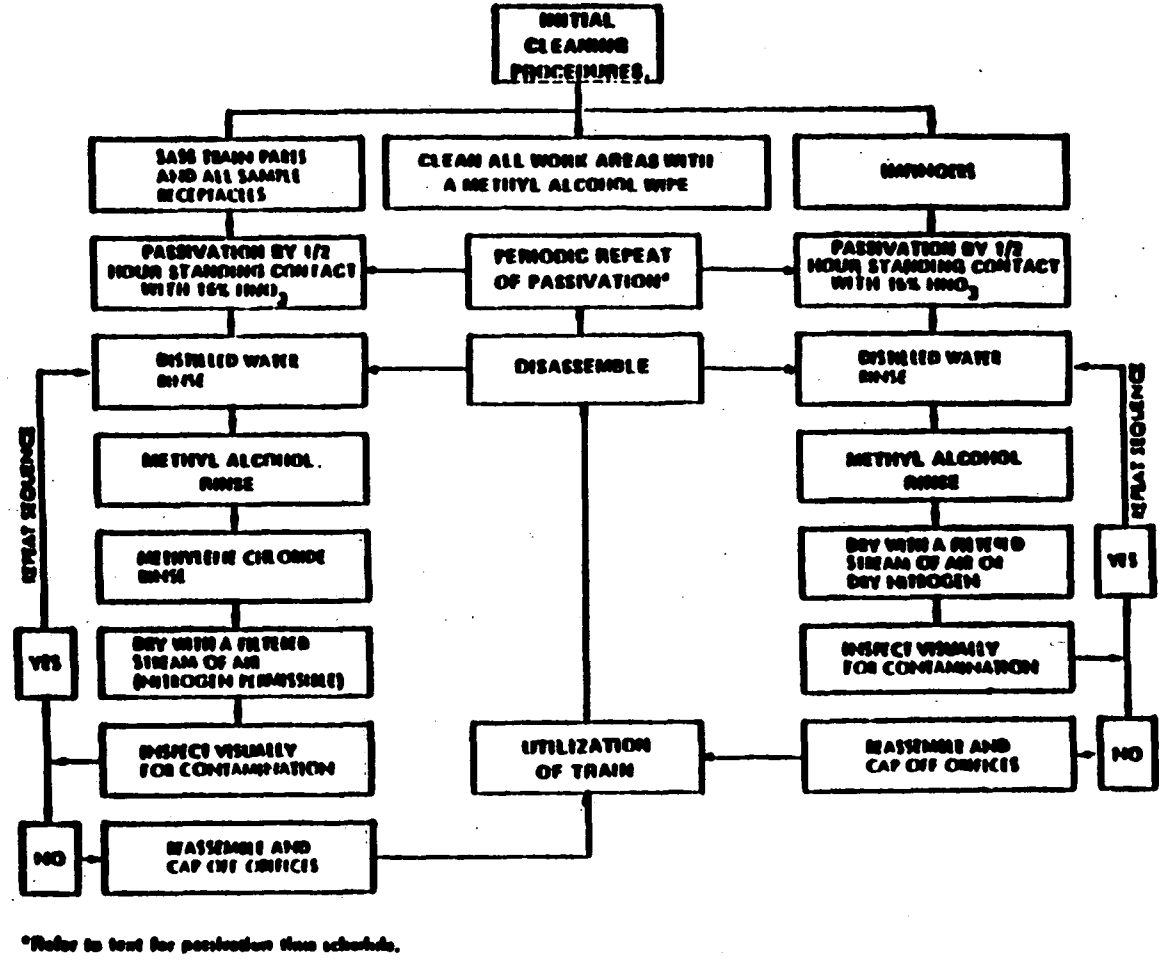
4.1.1 The probe tips, pitot tubes, dry gas meter, thermocouples, and any thermometers must be calibrated before and after each field sampling trip according to the procedures outlined in APTD-0576 (Rom, 1972) and below in Section 7.0. During extended sampling trips where the train will routinely be used more than 10 times, it is strongly recommended that a calibrated orifice, a set of micrometers (Vernier calipers), and a standard mercury-in-glass thermometer accompany the train to verify that the calibrations of the dry gas meter, probe nozzles, and thermocouples, respectively, have not changed significantly (more than ±2%). The aneroid barometer should be calibrated on a daily basis against a mercury barometer when in the laboratory and periodically in the field by consulting the local weather station and correcting for elevation (see Paragraph 7.7).

4.2 Laboratory preparation:

4.2.1 Weigh several 700- to 800-g portions of silica gel in airtight containers to ±0.1 g. Record the weight of the silica gel plus the container on the container and in a field sampling preparation notebook.

4.2.2 Holding with blunt-tipped tweezers, check filters visually against light for irregularities, flaws, or pinhole leaks. Label the shipping containers (glass Petri dishes) and keep the filters in these containers at all times except during sampling and weighing. The filters themselves need not be labeled if strict compliance with the above instruction is ensured. Desiccate the filters in a desiccator over Drierite or silica gel with the Petri dishes open at 20 ± 5.6°C (68 + 10°F) and ambient pressure for at least 24 hr and weigh. Thereafter weigh at 6-hr (minimum) intervals to a constant weight, i.e., previous weight ±0.5 mg; record the weight to the nearest 0.1 mg, along with the date and time, in the field sampling preparation notebook. Alternatively, the filters may be oven-dried at 105°C (220°F) for 2 to 3 hr, desiccated for 2 hr, weighed, and weighed thereafter at 6-hr intervals to a constant weight. During each weighing, the filter must not be exposed to the laboratory atmosphere for longer than 2 min with a relative humidity greater than 50%.

4.2.3 Passivate all SASS train parts and sample storage containers, referring to the procedure that appears in Figure 2, adapted from Level I requirements. Passivation is required of all new train components and sample storage containers before their initial use in the field. Thereafter, passivation should be conducted every 6 months when the frequency of tests is once per month or less, and every 3 months when the



SASS Cleaning Procedures

Source: "IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Ed.) EPA-600/7-78-201

Figure 2. SASS Cleaning Procedure

frequency is between once per week and once per month. If testing is more frequent, passivation should be conducted proportionately more often. Whenever corrosion has occurred, the corrosion must be removed and the passivation repeated. The passivation and rinse solutions should be replaced every fourth use, or discarded weekly.

4.2.4 Prepare recycled sample containers by detergent washing (using a stiff nylon brush where necessary), followed by rinsing with Type II water, methanol and methylene chloride. As each part is treated with the final solvent, dry with filtered air or dry nitrogen and inspect for any contaminating residue. Discard any container exhibiting visual contamination. Cover all open surfaces with aluminum foil or Teflon film, using elastic bands to secure.

4.2.5 Assembly and leak-checking of the entire train in the laboratory is highly recommended to reveal the need for replacement of gaskets or defective components. The leak-check procedure is described in Paragraph 4.4.3.11. Substitution of Viton-A gaskets for Teflon may facilitate meeting the allowable leak rate. A length of Teflon tape stretched around the circumference of each flanged connection underneath the ring clamp also greatly reduces inward air leakage.

4.3 Preliminary field determinations:

4.3.1 Select the sampling site and remove any accumulated scale and corrosion from the sampling portholes. Determine the stack static pressure, temperature, and velocity profile using EPA Method 2 (see References); a leak-check of the pitot lines prior to conducting these measurements is highly recommended. Approximate the moisture content using EPA Method 4 (Approximation Method) or alternate means such as drying tubes, wet bulb/dry bulb or condensation techniques, stoichiometric calculations, or previous experience. Determine the dry molecular weight of the stack gas by performing an ORSAT or GC/TCD analysis for CO, CO_2, O_2 and N_2 on an average of three grab samples taken from either the center of the duct or a point no closer to the stack walls than 1.0 m (3.3 ft).

4.3.2 Select a nozzle size based upon the calculations below, ensuring that it will not be necessary to change the nozzle during the sampling run to maintain near-isokinetic sampling rates.

4.3.2.1 To calculate the required nozzle diameter, first calculate the Average Stack Gas Velocity:

$$(V_s)_{avg} = K_p C_p (\sqrt{(\Delta P)})_{avg} \left[\sqrt{\frac{(T_s)_{avg}}{P_s M_s}} \right]$$

where:

$(V_s)_{avg}$ = Average stack gas velocity, ft/sec;

$$K_p = 85.48 \left[\frac{ft}{sec} \left[\frac{(lb/lb\text{-}mole)(in.\ Hg)}{{}^\circ R(in.\ H_2O)} \right]^{1/2} \right];$$

C_p = Pitot tube coefficient, dimensionless;

ΔP = Velocity head of stack gas, in. H_2O;

$(T_s)_{avg}$ = Average stack gas temperature, °R;

P_s = Absolute stack gas pressure, in. Hg; and

M_s = Molecular weight of stack gas (wet basis), lb/lb-mole.

4.3.2.2 Then calculate the required Nozzle Diameter (D_n):

$$D_n = 0.831 \sqrt{\frac{(T_s)_{avg}}{(V_s)_{avg} P_s}}$$

4.3.3 Select a suitable probe length such that one or more points of average velocity can be sampled. Determine the total length of sampling time by comparing the anticipated average sampling rate to the volume requirement of 30 dscm (approximately 1,060 dscf).

4.3.3.1 The anticipated Average Sampling Rate is calculated as follows:

$$Q_{mo} = (1-B_{ws})Q_{st} \frac{P_{st} (T_m)_{avg}}{P_m (T_{st})}$$

where:

Q_{mo} = Flow rate through orifice at meter conditions, ft^3/min (dry);

B_{ws} = Volume fraction of water vapor in the gas stream, dimensionless;

Q_{st} = Design sampling flowrate for SASS train, 4.0 scfm;

P_{st} = Standard presssure, 29.92 in. Hg;

$(T_m)_{avg}$ = Average gas temperature (estimated) at the dry gas meter, °R;

P_m = Absolute meter pressure, in. Hg, calculated by

$$P_m = P_b + \frac{(\Delta H)_{est.avg.}}{13.6}$$

where:

$(\Delta H)_{est.avg.}$ = Estimated average ΔH across orifice, 3-4 in. H_2O, and

P_b = Barometric pressure (corrected), in. Hg; and

T_{st} = Standard temperature, 528°R.

None of these definitions has an English/metric equivalent.

4.3.3.2 Using this result, obtain the approximate sampling time by dividing the required sample volume by the estimated sampling flowrate.

4.3.4 Finally, calculate the Orifice Pressure Drop needed to maintain near-isokinetic sampling conditions from the equation:

$$\Delta H_i = \frac{P_m}{(T_m)_{avg}} \left[\frac{0.1924\ Q_{mo}}{J_i D_{oi}^2}\right]^2$$

where:

ΔH_i = Required ΔH across the orifice, in. H_2O;

P_m = Absolute meter pressure, in. Hg (calculated the same way as for Average Sampling Rate above);

$(T_m)_{avg}$ = Estimated average gas temperature at the dry gas meter, °R;

J_i = Orifice coefficient for orifice "i" (see Blake, 1977, and Section 7.0 of this method for determining orifice coefficients); and

D_{oi} = Orifice diameter, in. (information supplied upon purchase of the SASS train; the largest diameter orifice is typically best suited for the SASS sampling rate of 4.0 scfm).

4.3.5 It is desirable, but not required, to sample more than one point of average velocity during a SASS run. Allocate equal intervals of the total sampling time estimated above to each sampling point chosen if more than one point will be sampled.

4.4 Preparation of collection train:

4.4.1 An integral part of preparing the collection train is securing sufficient electrical power to operate for an extended period of time without interruption. Three separate circuits -- two 30-amp and one 20-amp -- are required. It is highly recommended that one sampling pump and one control box power cord (probe heater) be placed on one of the 30-amp circuits, and the other sampling pump and control box power cord (oven heater and temperature readout) be placed on the other 30-amp circuit. The organic module coolant pump and temperature controller should be placed on the smaller 20-amp circuit.

4.4.2 During assembly of the train, keep the inner surfaces of each component covered until it is integrated into the system and sampling is about to begin. Fill the sorbent trap section of the organic module with approximately 150 g of clean adsorbent XAD-2 resin. To avoid contamination, the trap should be placed upon a clean surface (i.e., aluminum foil rinsed with methylene chloride and air-dried) while filling; gloves should be worn. Pack the trap uniformly to eliminate potential channeling. Place 500 mL of Type II water or other appropriate solution into the first and second impingers, leave the third impinger empty, and place a preweighed portion of silica gel into the fourth.

NOTE: The choice of impinger solutions depends upon whether these will be used to collect selected inorganic species or simply to condense water vapor from the gas stream to measure percent moisture. For example, in an incinerator combusting chlorinated organic material, a solution of dilute base would typically be used to collect hydrochloride acid emissions.

Using blunt-tipped tweezers, place a tared filter into the filter holder. Ensure that the filter is centered and the gasket properly placed to prevent the gas stream from circumventing the filter. On the probe, mark the locations of the chosen sampling points with heat-resistant tape or paint.

4.4.3 The stepwise procedure for assembly of the train follows:

4.4.3.1 Place the oven on a table or rollers that will be used as a support throughout the run.

4.4.3.2 Assemble the three cyclones, using the vortex breaker supplied with the cyclone in the 10-um cyclone only. (To minimize leaks throughout the system, a strip of Teflon tape should be stretched around the circumference of each flanged seal and the ring clamp placed over and secured.) Do not use the vortex breakers supplied with the 3- and 1-um cyclones in the 3- and 1-um cyclones. Actual calibration data has shown that the use of the vortex breakers in the two smaller cyclones may result in unreproducible particle-size cutoff diameters (the particle size at which 50% collection efficiency is exhibited).

4.4.3.3 Attach the filter holder to the outlet of the 1-um cyclone and place the cyclones and filter holder together in the oven. Preheat a spare filter holder containing a tared filter on the oven floor; cover the holder openings with aluminum foil.

4.4.3.4 Attach the probe to the oven and to the 10-um cyclone.

4.4.3.5 Place the impingers in the tray in the impinger case and make the apropriate interconnections.

4.4.3.6 Connect the organic module inlet to the filter housing outlet and the organic module outlet to the first impinger inlet.

4.4.3.7 Connect the vacuum pumps in parallel to the fourth impinger outlet.

4.4.3.8 Connect all temperature sensors and power lines to the control unit. Check temperature indicators and controllers at ambient temperature.

4.4.3.9 Activate gas cooling system. Begin monitoring the XAD-2 temperature. Always check coolant level before supplying power. Ensure proper gas cooling system temperature before proceeding.

NOTE: IT IS EXTREMELY IMPORTANT THAT THE XAD-2 RESIN TEMPERATURE NEVER EXCEED 50°C, AS DECOMPOSITION WILL OCCUR. DURING TESTING, THE XAD-2 TEMPERATURE MUST NOT EXCEED 20°C FOR EFFICIENT CAPTURE OF THE SEMIVOLATILE ORGANIC SPECIES OF INTEREST.

4.4.3.10 Heat oven and probe to 204°C (400°F).

4.4.3.11 Run gas flow leak-check. The following instructions will facilitate the leak-checking procedure:

a. Open the isolation ball valve and plug the inlet to the probe with a rubber stopper or appropriate airtight cap.

b. Start the pumping system with the bypass valves fully open and the coarse valves completely closed. Partially open the coarse valves and slowly close the bypass valves until a vacuum of 127 mm Hg (5 in. Hg) is reached. Do not reverse the direction of the bypass valves as backflushing of the impinger solutions into the organic module will result. If the desired vacuum is exceeded, either leak-check at the higher vacuum or terminate the leak-check and begin again. Allow the system to equilibrate and measure the leakage rate. The allowable leak rate for the SASS train is 0.0014 m^3/min (0.05 ft^3/min) at this vacuum. Close the isolation ball valve and evacuate the train to 281 mm Hg (15 in. Hg). The leak rate through the back half of the train should be less than 0.0014 m^3/min (0.05 ft^3/min) at this vacuum.

c. When the leak-check is complete, slowly remove the plug from the probe tip and then slowly open the isolation ball valve.

d. When the vacuum drops to 127 mm Hg (5 in. Hg) or less, immediately close both coarse control valves together. Switch off the pumping system and reopen the bypass valves. The bypass valves should not be opened until the coarse valves have been closed.

4.4.4 Only post-test leak-checks are mandatory; however, experience has shown that pre-test leak-checks and leak-checks following component changes are necessary to ensure that invaluable sampling time is not lost as a result of an oversight or defective component.

4.5 Sample Collection: Constant monitoring of train operations before, during, and after the particulate run is essential in maintaining sample integrity. Listed below are sample collection guidelines:

4.5.1 With the coarse valves closed and bypass valves open, turn on the vacuum pumps and allow them to warm up. As the probe and oven are heating, prepare a SASS run data sheet as shown in 40 CFR Appendix A (see References below). Barometric pressure data should be recorded at least at the beginning and end of the run; once per hour is preferred.

4.5.2 When operating temperatures have been reached, place the probe in the stack at the first designated sampling point, turn on the vacuum pumps, adjust the sampling flowrate to achieve the calculated ΔH_i, and start the elapsed timer. If, however, the gas stream is under medium or high negative pressure, it becomes extremely important to start the vacuum pumps just before placing the probe in the gas stream, and to continue to operate the pumps until just after the probe has been removed from the gas stream. This will eliminate the possibility of lifting of the filter or backflushing of the filter and cyclone particulate catches at any time.

4.5.3 Seal the sampling port around the probe to prevent introduction of dilution air at this point. Record the clock time of the start of the test.

4.5.4 Using the criteria outlined above under Paragraph 4.3, Preliminary Field Determination, place the integrated fixed gas bag or bulb sampling probe into the gas stream and begin sampling. Collect three samples during the SASS run; record the initial and final clock times of each integrated fixed gas sample.

4.5.5 Monitor and maintain all temperatures and the calculated ΔH and record the data at equal intervals of 10-15 min.

4.5.6 Add crushed ice to the impinger section and drain excess water as necessary.

4.5.7 Without interrupting sampling, drain the condensate initially every 30-45 min, and afterward as necessary. Ensure that the vessel into which the reservoir is drained forms an airtight system with the reservoir using a connecting Teflon line, and is placed well below the level of the reservoir itself. To drain the reservoir, close the solation ball valve and open the drain valve. Allow the system to evacuate for 10-20 sec. Carefully open the isolation valve. The condensate should siphon from the reservoir into the storage vessel. Close the drain valve when the siphoning action of the condensate ceases.

4.5.8 Replace the filter when it becomes impossible to maintain near-isokinetic sampling rates but not more frequently than every 20 to 30 min. Always terminate and initiate sampling by adjustment of the coarse pump valves and then the bypass valves. A spare filter holder and filter, if available, should be preheating in the oven at all times. Conduct leak-checks before and after changing the filter. Recall previous instructions concerning removal and reintroduction of the probe into the duct.

4.5.9 At the same time, check the 1-um cyclone reservoir for remaining capacity, taking care not to contaminate the contents during this inspection.

4.5.10 When replacing a filter, start and stop the fixed gas sampling concurrently with the SASS sampling; record the clock time and dry-gas-meter reading whenever sampling is interrupted.

4.5.11 Upon collection of the required 30 dscm (1,060 dscf), remove the probe from the gas stream and shut down the pumps as previously instructed. Record the final dry-gas-meter reading and clock time; turn off all heaters. Conduct the post-test leak-check when the probe tip can be safely handled. Do not cap the probe while initially cooling, because this will create a vacuum inside that will cause disruption of the cyclone and filter particulate catches when it is released. Instead, use aluminum foil to cover probe openings. Before the probe is transported, secure the aluminum foil covers with elastic bands. Leak-check the pitot lines per EPA Method 2 to validate velocity heat data.

5.0 SAMPLE RECOVERY

The sample handling and transfer procedures outlined in this section have been adopted from the Level 1 procedures. The flow diagrammatic representation of the sample recovery procedures shown in Figures 3, 4, and 5 can be found in the Level 1 Sampling and Analysis Procedures Manual.

5.1 Disassembly of the SASS Train: At the conclusion of the sampling run, the train is disassembled and transported to the prepared work area as follows:

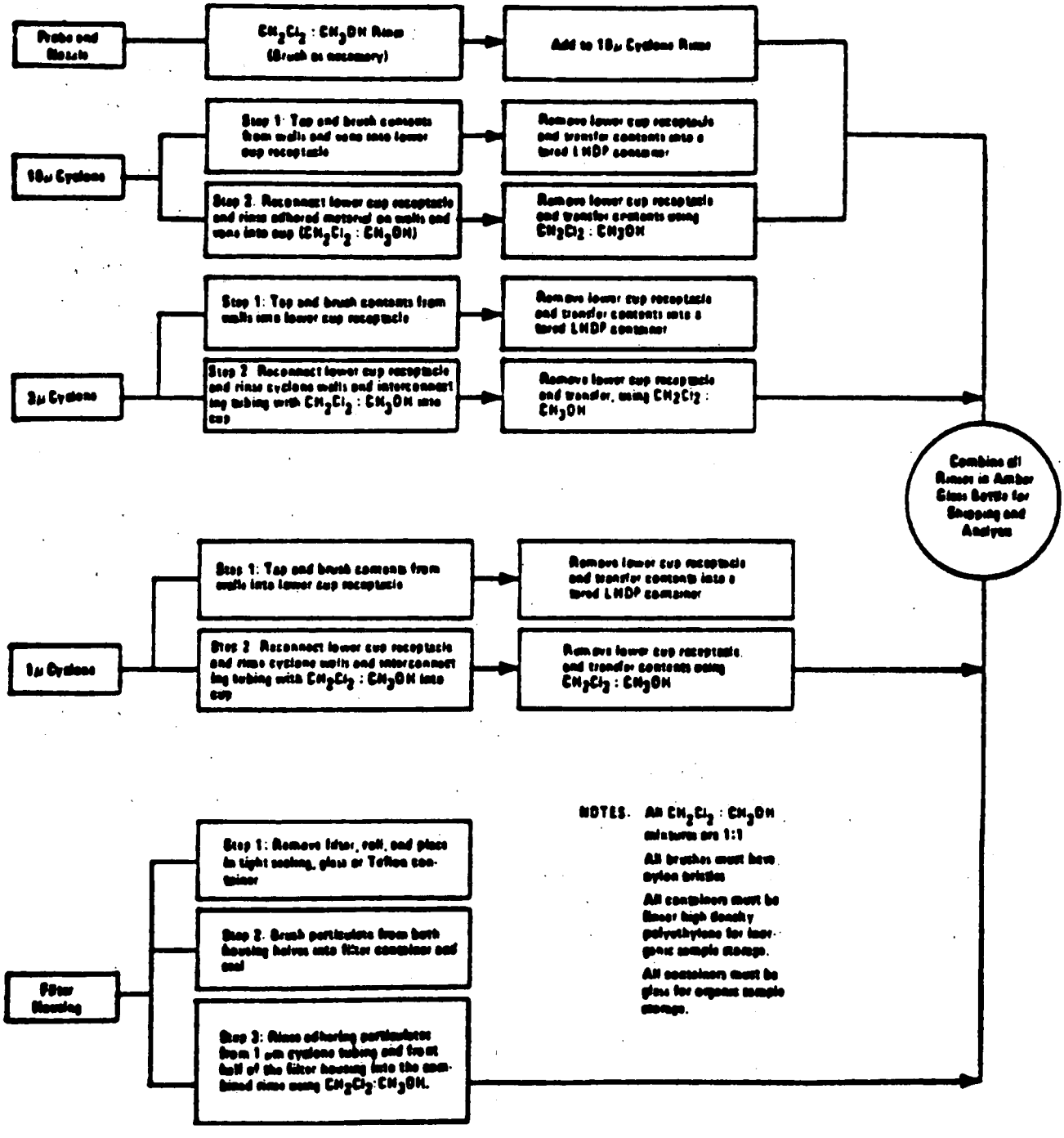


Figure 3. Sample Handling and Transfer Nozzle, Probe, Cyclones and Filter.

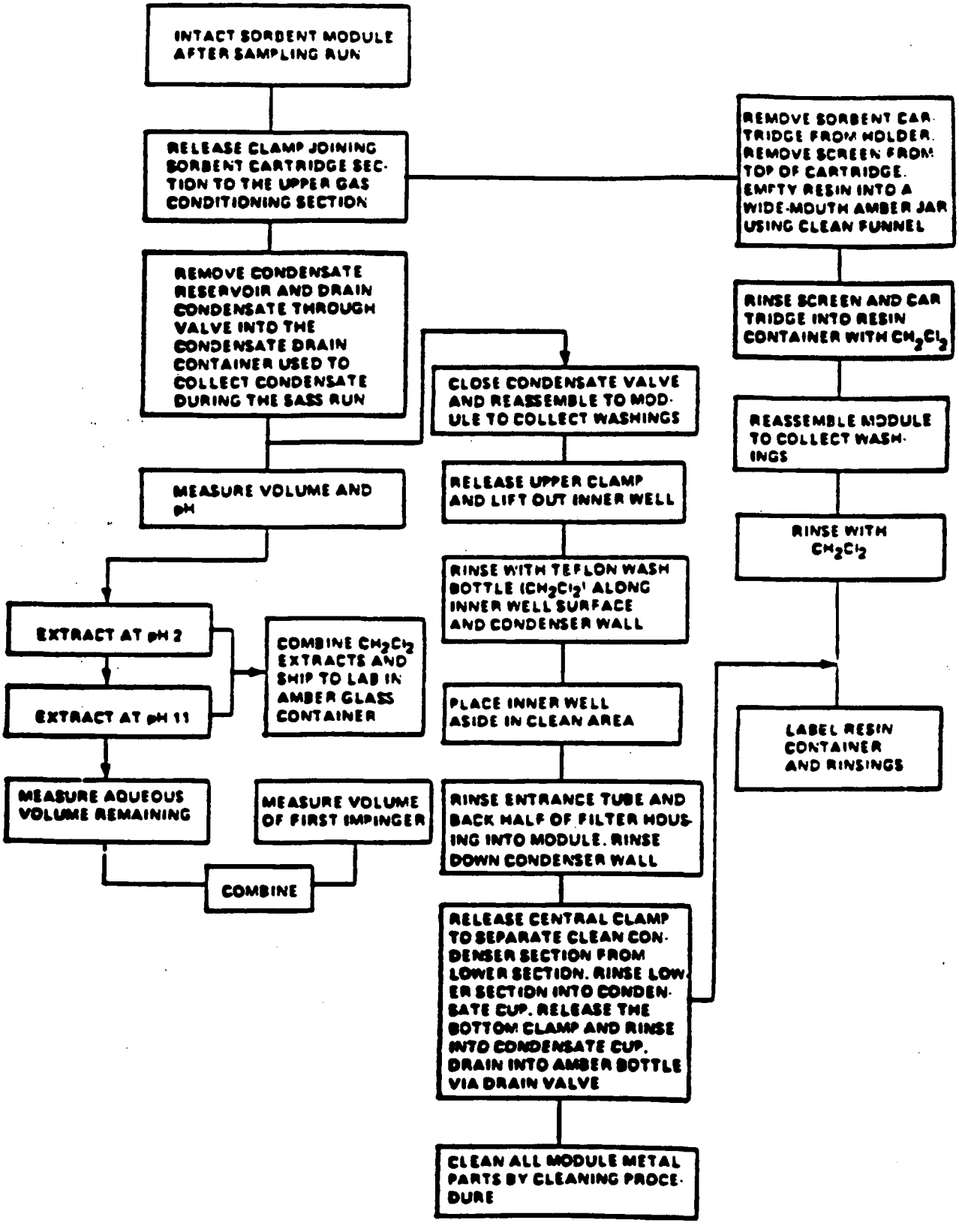


Figure 4. Sample Handling and Transfer XAD-2 Module.

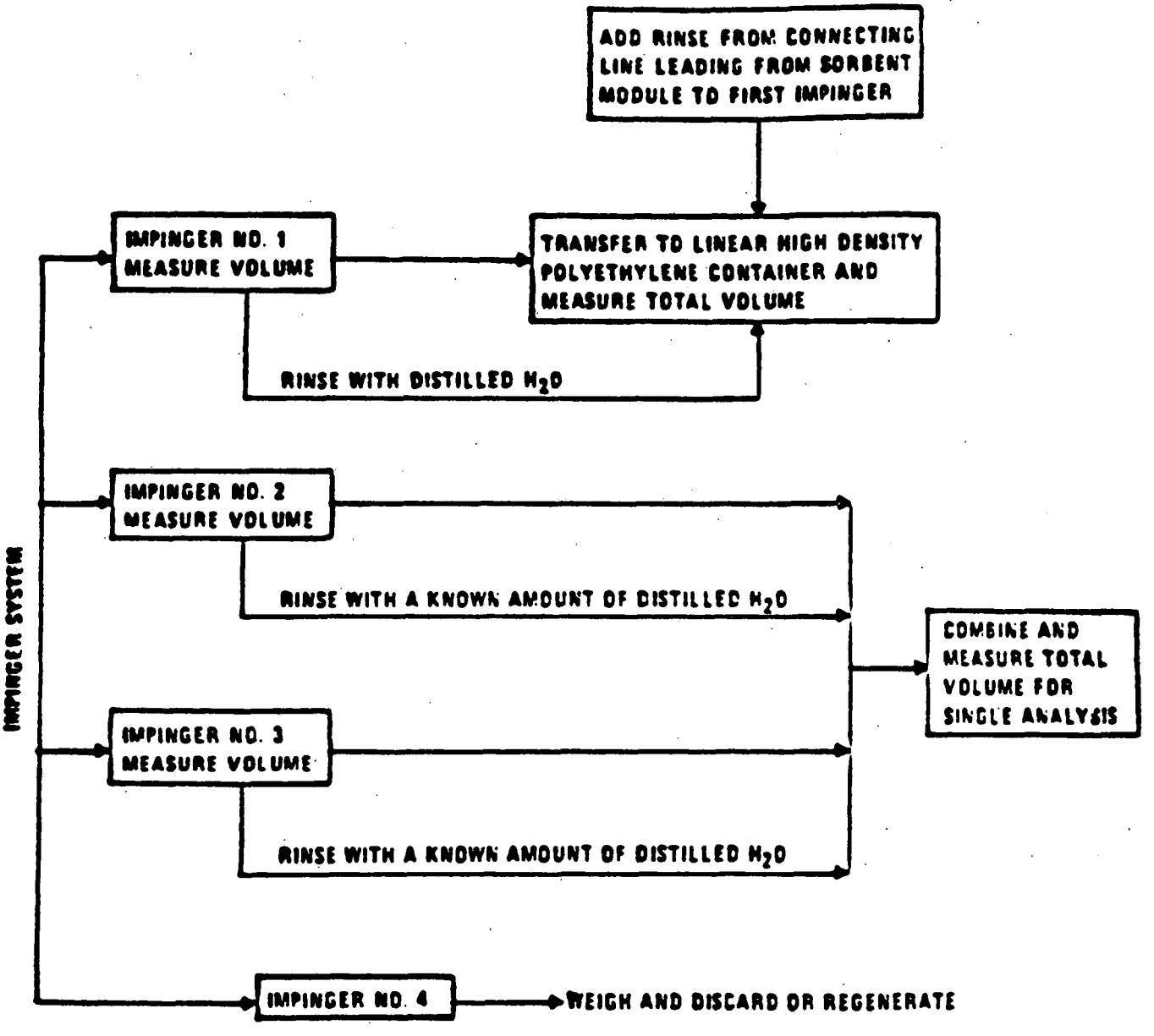


Figure 5. Sample Handling and Transfer Impingers.

5.1.1 Leaving the fan operating, open the cyclone oven door to expedite cooling. When the probe can be safety handled, disconnect from the 10-um cyclone inlet. Wipe off external particulate matter near the probe tip and place a cap over each end. The probe must remain level throughout this procedure.

NOTE: CARE MUST BE TAKEN TO AVOID TIGHTLY CAPPING TRAIN COMPONENTS AS THEY ARE COOLING FROM STACK OR OVEN TEMPERATURES. THIS WILL ELIMINATE THE POSSIBILITY OF CREATING A VACUUM INSIDE WHICH, WHEN RELEASED, MAY DISRUPT AND BACKFLUSH THE CYCLONE AND FILTER PARTICULATE CATCHES INTO ONE ANOTHER.

5.1.2 Disconnect the line joining the filter outlet to the XAD-2 module and cap off:

a. The 10-um cyclone inlet;

b. The filter holder outlet; and

c. The inlet of the line just disconnected from the filter holder outlet.

5.1.3 Disconnect the filter holder and cap the inlet. Set aside with the inlet facing upward. Cap the outlet of the 1-um cyclone. The cyclones must remain upright throughout this procedure. The cyclones can now be disconnected from one another or moved to the recovery area as a single unit.

5.1.4 Disconnect the line joining the XAD-2 module to the impinger system at the organic module outlet. Cap the organic module outlet.

5.1.5 Disconnect the silica gel impinger outlet from the vacuum line to the pumps; cap off the first impinger inlet and the fourth impinger outlet.

5.2 Nozzle, Probe, Cyclones, and Filter: The step-by-step procedures for the recovery of particulate material collected in the nozzle, probe, and cyclones, and on the filter are detailed below:

5.2.1 Carefully transfer the filter from the filter housing to its original glass Petri dish; a pair of clean blunt-tipped tweezers and a flat spatula should be used for handling the filter. Using a clean nylon-bristled brush, add any particulate material from the front half of the filter housing to the Petri dish; seal the Petri dish around the circumference with 1-in.-wide Teflon tape; store with the collected particulate material facing upward.

5.2.2 Tap and brush any particulate material adhering to the walls of the upper chamber of the 1-um cyclone into the lower cup; remove the cup and quantitatively transfer the bulk contents to a wide-mouth amber glass jar. Rinse the brush with methanol/methylene chloride (1:1 v/v) into the probe rinse container.

5.2.3 Recover the contents of the 3-um cyclone in the same manner, using a separate wide-mouth amber glass jar.

5.2.4 Recover the contents of the 10-um cyclone in the same manner, using a separate wide-mouth amber glass jar.

5.2.5 Reconnect the lower cups of each cyclone and rinse any particulate material adhering to the walls down into the cups with the methanol/methylene chloride mixture until the walls appear clean. Remove the lower cups and transfer the contents to the probe rinse container. Rinse the interconnecting tubing among the cyclones into the probe rinse in the same manner.

5.2.6 Carefully remove the probe nozzle and clean the inside surface by rinsing with the methanol/methylene chloride (1:1 v/v) from a wash bottle and brushing with a nylon-bristle brush. Brush until the rinse shows no visible particles; make a final rinse of the inside surface.

5.2.7 Rinse the probe liner (preferably with two people so as to minimize the possibility of accidental sample loss) with methanol/methylene chloride (1:1 v/v) by tilting and rotating while spraying solvent into the upper end and allowing the lower end to drain into the sample container. Follow rinsing with brushing and rinsing from the upper to the lower end. Push the brush through the liner with a twisting action; ensure that the sample container is placed under the lower end. Brush until the rinse appears clean; perform a final rinse. Inspect the inner surface of the liner for cleanliness. Rinse any particulate material remaining on the brush into the sample container.

5.2.8 Clearly label all containers according to the coding scheme given in Table 1; cover each label completely with transparent tape; mark liquid levels and store all liquid samples on ice.

5.3 XAD-2, condensate, and organic module: Sample recovery of the entire organic module may be conducted independently from the previous steps. The step-by-step procedure for recovery of this stage is given below:

5.3.1 Rinse a 1-ft x 1-ft square of aluminum foil (dull side) with methylene chloride and allow to air dry.

5.3.2 Release the clamp joining the XAD-2 cartridge section to the upper gas conditioning system (second clamp); remove the XAD-2 cartridge from the holder and place upon the clean aluminum foil. GENTLY pry loose or unscrew (depending upon the design) the ring securing the fine mesh screen on the top of the cartridge. Remove the screen and quantitatively transfer the XAD-2 to a clean glass amber jar. A large, clean glass funnel should be used for the transfer. Rinse the inner surfaces of the cartridge and the funnel with methylene chloride as necessary to remove adhering XAD-2. Any XAD-2 that escapes onto the aluminum foil should be retrieved and added to the sample.

TABLE 1. SUGGESTED FORMAT FOR SAMPLE CODING AND IDENTIFICATION

Sample Code	Container	Size	Sample description
1C	Amber glass	100 mL, wide-mouth	1-m cyclone catch
3C	Amber glass	100 mL, wide-mouth	3-m cyclone catch
10C	Amber glass	100 mL, wide-mouth	10-m cyclone catch
PF-a,b,c,...	Glass Petri dish	>6-in. diam.	Particulate filter(s)
PR	Amber glass	1 liter	Methylene chloride/ methanol front-half rinse
PRB	Amber glass	500 mL	Methylene chloride/ methanol blank
MRX	Amber glass	1 liter	Methylene chloride back half rinse
MRXB	Amber glass	500 mL	XAD-2 resin blank
CD-LE	Amber glass	1 liter	Methylene chloride condensate extract
CD-LEB	Amber glass	500 mL	Methylene chloride blank
AR-I1	HDLP[a]	1 liter	Aqueous residue of condensate combined with first impinger catch
I1B	HDLP	500 mL	First impinger blank (distilled H_2O or other appropriate solution)
I23	HDLP	1 liter	Second and third impinger catches
I23B	HDLP	500 mL	Second and third impinger blank (distilled H_2O or other appropriate solution)

[a]HDLP = High Density Linear Polyethylene.

5.3.3 Replace the screen on the cartridge, reinsert the cartridge into the module, and reassemble the module. One person can accomplish this task by butting the lower section in its proper sealing position up against the upper section while securing the ring clamp. One or more wooden spacers approximately 1/2 in. thick are suggested for this purpose.

5.3.4 Open the condensate reservoir valve and drain the remaining condensate into the condensate storage container. Measure and record the volume and pH (using narrow-range pH paper) of the entire condensate.

5.3.5 Transfer the entire condensate to an appropriately-sized separatory funnel. Adjust the pH of the condensate (as indicated by the narrow-range pH paper) to 1-2 using ultrapure or reagent grade nitric acid. Extract the condensate three times with methylene chloride, each time with fresh portions measuring 8-10% of the total condensate volume. If the volume of the condensate is extremely large (>1800 mL), the condensate may be extracted in portions, but fresh volumes of methylene chloride must be used for each and every extraction. After each addition of methylene chloride to the separatory funnel, the funnel must be shaken with periodic venting through the stopcock to relieve any vapor pressure. For safety, the tip of the separatory funnel should always be directed away from the face and eyes while venting. When no further vapor pressure can be vented after shaking, the funnel should be mounted upright on a ring stand, the cap removed, the layers allowed to separate, and the methylene chloride (bottom) layer removed. If an emulsion forms equal to more than one-third the size of the solvent layer, reagent-grade sodium chloride should be added until the emulsion is broken or reduced to meet the above criterion. The emulsion interface should not be included as part of the methylene chloride extract.

5.3.6 Following the third extraction of the acidified condensate, adjust the pH of the aqueous residue to 11-12 with a 50% w/w solution of sodium hydroxide (as indicated by narrow-range pH paper), extract with methylene chloride in the same manner, and combine the methylene chloride extracts of the condensate at the high and low pH readings.

5.3.7 Transfer the aqueous residue from this extraction to a clean Nalgene container; retain for later addition of the first impinger solution.

5.3.8 Ensure that the condensate reservoir valve is closed, release the upper clamp, and lift the inner well halfway out of the module. Rinse the inner well into the XAD-2 module using a Teflon wash bottle containing methylene chloride, so that the rinse travels down the module and into the condensate collector. Then remove the well entirely and place to one side on a clean surface (aluminum foil prerinsed with methylene chloride). Rinse the entrance tube into the module interior; rinse the condenser wall allowing solvent to flow down through the system and collect in the condensate cup.

5.3.9 Release the central clamp again and separate the lower section (XAD-2 cartridge holder and condensate cup) from the upper.

5.3.10 Lift the empty XAD-2 cartridge halfway out of the mid-section and rinse the outer surface down into the condensate cup. Remove the cartridge completely to a clean surface (aluminum foil rinsed with methylene chloride).

5.3.11 Rinse the empty XAD-2 section into the condensate cup. Open the condensate reservoir valve and drain into the XAD-2 sample storage container (wide-mouth amber glass jar).

5.3.12 Rinse the condensate reservoir and combine the rinse with the XAD-2 resin as above.

5.3.13 Clearly label all containers according to the coding scheme presented in Table 1; cover each label completely with transparent tape; mark liquid levels and store all liquid samples on ice.

5.4 Impingers: Sample recovery from the impingers may also be accomplished independently of the other two sections of the SASS train. The procedures are described below.

5.4.1 **First impinger:**

5.4.1.1 Measure the volume of liquid in the impinger with a graduated cylinder; combine with the aqueous residue from the condensate.

5.4.1.2 Rinse the line connecting the XAD-2 module to the first impinger with Type II water; transfer the rinse to the same graduated cylinder. Rinse the impinger twice more with Type II water, combining all rinses in the graduated cylinder. Measure the total rinse volume and add to the sample. Rinse the graduated cylinder with a known amount of Type II water and add to the sample. Record all volumes on the sample recovery sheet.

5.4.2 **Second and third impingers:**

5.4.2.1 Measure and record the combined volume of liquid in the impingers in a large (1,000-mL) graduated cylinder; transfer to a clean sample storage container.

5.4.2.2 Rinse the line connecting the first and second impinger into the second impinger and the line connecting the second and third impinger into the third impinger. Transfer the rinses to the same graduated cylinder. Rinse each impinger twice again with Type II water, combining all rinses in the graduated cylinder. Measure and record the combined rinse volume and add to the sample. Rinse the graduated cylinder with a known amount of Type II water and add to the sample. Record this additional rinse volume and add to the impinger rinse volume above.

5.4.2.3 Clearly label all sample containers according to the coding scheme presented in Table 1; cover each label completely with transparent tape; mark fluid levels and store all liquid samples on ice.

5.4.3 **Fourth impinger:**

5.4.3.1 Transfer the silica gel to its original container. Weigh to the nearest 0.1 g on a triple-beam balance, and record the weight.

5.4.3.2 Discard or regenerate.

6.0 SAMPLE PREPARATION FOR SHIPMENT

6.1 Prior to shipment, recheck all sample containers to ensure that the caps are securely tightened. Seal the lids of all Nalgene containers around the circumference with vinyl tape and those of glass containers with Teflon tape. Ship all liquid samples on ice and all particulate filters with the particulate catch facing upward. Ship peroxide solutions (impinged) in a separate container.

7.0 CALIBRATION

7.1 All calibration results should be recorded on appropriate data sheets and fastened securely into a separate section in the field sampling notebook. Samples of blank data appear in 40 CFR 60 (1979), Appendix A.

7.2 Probe nozzles:

7.2.1 Probe nozzles must be calibrated before each initial use in the field. Using Vernier calipers or micrometers, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Perform ten separate measurements using different diameters; obtain the average of the ten measurements. The difference between the highest and lowest measurement results must not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they must be reshaped, sharpened, and recalibrated before reuse. Recalibration of the nozzle before each run in gas streams that are highly corrosive is strongly recommended, as the nozzle diameter may be changing slightly from one run to the next. Each nozzle must be permanently and uniquely engraved.

7.3 Pitot tube

7.3.1 If the Type-S pitot tube conforms to the construction specifications (the face openings are not visibly nicked, dented, or corroded) and the pitot tube/probe assembly meets the intercomponent spacings outlined in EPA Method 2 (see References), the pitot tube need not be calibrated to meet federal and many state testing requirements; a correction coefficient may be assigned in these cases. Some states, however, require that, once used, pitot tubes must be calibrated in a

wind tunnel. Specific state requirements such as this must be unequivocally stated prior to testing. In either case, pitot tube face openings should be inspected before each run to ensure that there has been no change in appearance since their construction or most recent calibration.

7.4 Metering system:

7.4.1 Before each initial use in the field, the metering system shall be calibrated using a standard bell prover of the proper size. (A standard bell prover is recommended for this procedure because the displacement volume of commercially available wet test meters is typically insufficient.) A meter stick should be used to indicate the distance travelled by the inner tank during the measurement. Figure 6 illustrates a suitable arrangement for the calibration. It is highly recommended that the dry gas meter be adjusted until the ratio of the dry gas meter volume to the standard bell prover volume equals 1.00 $\pm$ 0.01, to ensure that the calculated ΔH_i will result in near-isokinetic sampling rates. The calibration procedure follows:

7.4.1.1 Perform both a positive (pressure) and a negative (vacuum) leak-check of the metering system. For the negative leak-check, include only the orifice Magnehelics (reg. trademark), dry gas meter, and two vacuum pumps by removing the vacuum line connecting the fourth impinger to the vacuum pumps at the common side of the pump inlet tee, and replacing the line with a plain-end male quick connect. Tightly cap this end and leak-check in the manner outlined above under 4.4.3.11. For the positive leak-check, connect a short length of rubber tubing to the "gas exhaust" port on the SASS control module. Disconnect and vent the low side of the orifice magnehelic; close off the low-side orifice tap. Pressurize the system to 13-18 cm H_2O (5-7 in. H_2O) by blowing into the rubber tubing; pinch off the tubing and observe the magnehelic for one minute. The magnehelic reading must remain unchanged during that time period. Any loss of magnehelic pressure indicates a leak that must be corrected.

7.4.1.2 Upon obtaining satisfactory leak-checks, connect the metering system to the standard bell prover.

7.4.1.3 Using the control box Magnehelic (reg. trademark) indicator, set the pumping rate corresponding to a ΔH of 1 in. Hg. Turn the pumps off using the switches.

7.4.1.4 Record the initial temperature and pressure of the bell prover and the initial temperature and reading of the dry gas meter. Record the barometric pressure every hour.

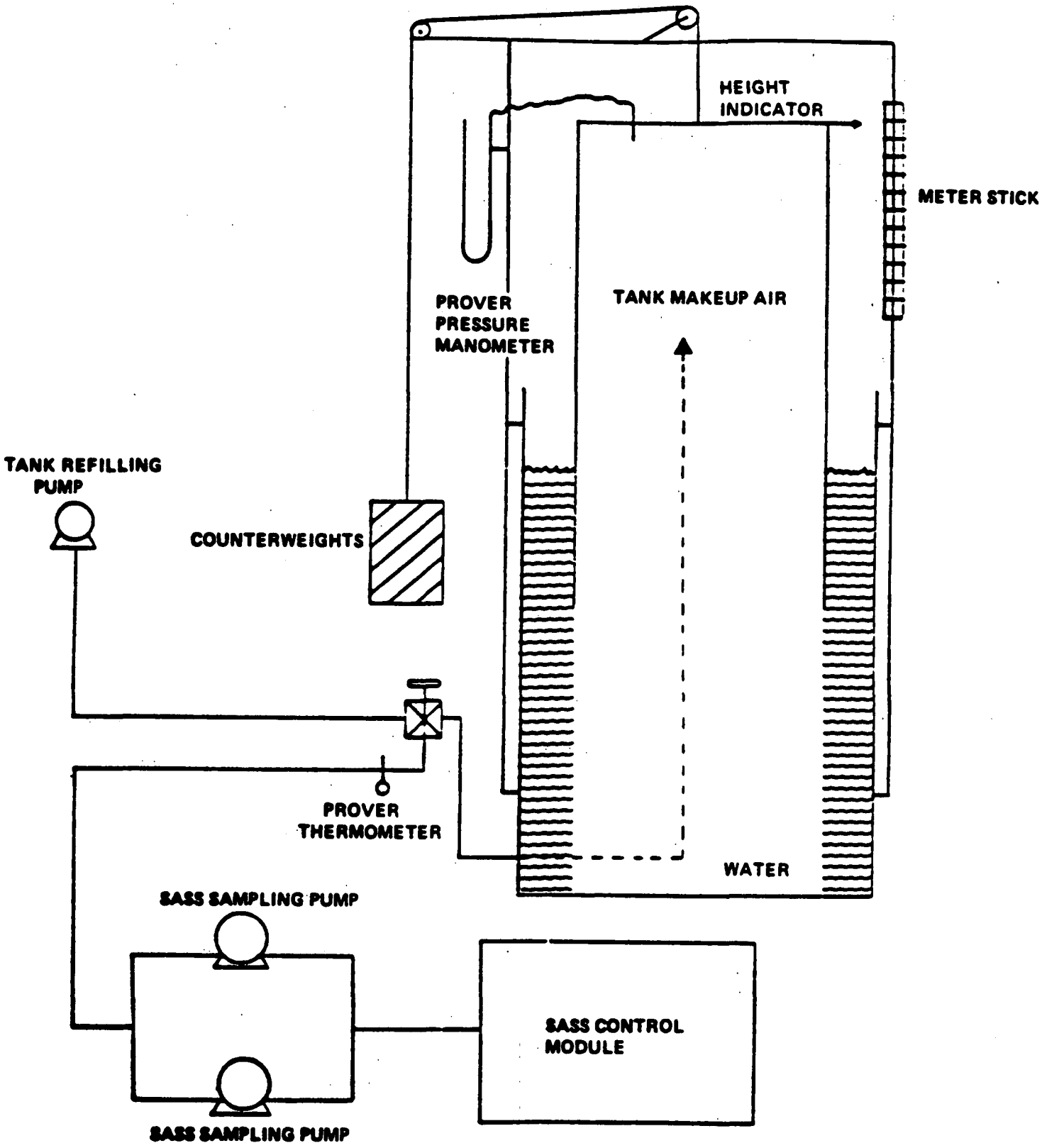


Figure 6. Schematic Diagram of Standard Bell Prover Arrangement for SASS Dry-Gas-Meter Calibration.

7.4.1.5 Disconnect the metering system and pump the inner tank of the bell prover to a convenient height. Reconnect the metering system and record the height.

7.4.1.6 Start the pumps and a stopwatch simultaneously; evacuate the tank for 3 min.

7.4.1.7 After 3 min, turn off the pumps using the switches. Record the final inner tank height, the final dry gas meter reading and temperature, and the bell prover final temperature and pressure.

7.4.1.8 Repeat steps 3-7 using ΔH settings of 2, 4, and 6 in. H_2O.

7.4.1.9 Duplicate the entire procedure as a check; repeat the entire procedure after each adjustment of the dry gas meter.

7.4.1.10 Calculate the Dry-Gas-Meter Correction Coefficient, the ratio of the volume of gas measured by the dry gas meter to the standard bell prover, both corrected to standard conditions and on a dry basis. The ratio reduces to:

$$\gamma = \frac{V_{pvr(std)}}{V_{dgm(std)}} = \frac{V_{pvr} P_{pvr} T_{dgm}}{V_{dgm} P_{dgm} T_{pvr}}$$

where:

γ = Dry gas meter correction coefficient, dimensionless;

$V_{dgm(std)}$ = Volume of gas measured by the dry gas meter on a dry basis, corrected to standard conditions, dscm (dscf);

$V_{pvr(std)}$ = Volume of gas measured by the standard bell prover on a dry basis, corrected to standard conditions, dscm (dscf);

V_{dgm} = Volume of gas measured at dry-gas-meter conditions, $m^3(ft^3)$;

= Final volume reading - initial volume reading;

V_{prv} = Volume of gas measured at standard bell prover conditions, $m^3(ft^3)$

= K_{pvr} x (difference in meter stick height readings),

where:

K_{pvr} = number of ft^3 of air displaced represented by each cm of movement along the meter stick, $m^3/cm(ft^3/cm)$;

P_{dgm} = Absolute meter pressure, mm Hg (in. Hg)

= Barometric pressure + ΔH/13.6;

P_{pvr} = Absolute prover pressure, mm Hg (in. Hg)

= Barometric pressure - [(ΔP) prover manometer]/13.6;

T_{pvr} = Absolute bell prover temperature, °K (°R); and

T_{dgm} = Absolute dry-gas-meter temperature, °K (°R).

7.4.1.11 Calculate the Orifice Constants using the following equations:

a. $$Q_{mo} = (1-B_{ws})\ Q_{std}\ \frac{P_{std}T_{m(avg)}}{P_m T_{std}}$$

where:

Q_{mo} = Sampling flowrate at orifice, ft^3/min (dry);

B_{ws} = Proportion by volume of water in ambient air, dimensionless;

Q_{std} = Standard sampling flowrate for SASS, 4.0 scfm (wet);

P_{std} = Standard absolute pressure, 29.92 in. Hg;

$T_{m(avg)}$ = Average meter temperature, °R;

P_m = Absolute meter pressure (barometric pressure + ΔH/13.6), in. Hg; and

T_{std} = Standard temperature, 528°R.

b. $$J_i = \frac{Q_{mo}}{A_{oi}} \left[\frac{T_{m(avg)}}{P_m M_m}\ R\Delta H_i 2g_c \right]^{-1/2}$$

where:

J_i = Orifice coefficient for orifice "i";

Q_{mo} = Sampling flowrate at orifice, ft^3/min (dry);

A_{oi} = Orifice area $[\pi(\text{diameter})^2]/4$, $in.^2$;

$T_{m(avg)}$ = Average meter temperature, °R;

P_m = Absolute meter pressure (see equation above), in. Hg;

M_m = Molecular weight of air, 29.0 lb_m/lb-mole;

R = Gas law constant, 1545 ft-lb_f/°R lb-mole;

ΔH_i = Orifice "i" pressure drop, in. H_2O; and

g_c = Gravitational constant, 32.17 lb_m-ft/lb_f sec^2.

7.4.1.12 The orifice constants may be determined without the bell prover by noting the dry-gas-meter volumes obtained by pumping at 1, 2, 3, and 6 in. H_2O for 3-min periods. The obtaining of consistent values when checking orifice constants in the field may be used as a rough indication of a valid calibration during extended field use.

7.4.2 After each series of field tests, the calibration of the metering system must be checked by performing three calibration measurements at a single intermediate orifice setting at or near the average used during the field testing. If the calibration has changed by more than 5%, recalibrate the meter over the full range of orifice settings. Calculations for the test series should then be performed using whichever calibration results in the lower value for total sample volume.

7.5 Probe heater: The probe heating system shall be calibrated before each initial use in the field and checked after each series of field tests according to the procedure outlined in APTD-0576.

7.6 Thermocouples: Each thermocouple must be permanently and uniquely marked on the casing; all mercury-in-glass reference thermometers must conform to ASTM-E-1 #63C or 63F specifications. Thermocouples should be calibrated in the laboratory without the use of extension leads. If extension leads are used in the field, the thermocouple reading at ambient air temperatures, with and without the extension lead, must be noted and recorded. Correction is necessary if the use of an extension lead produces a change greater than 1.5%. Calibration for the various kinds of thermocouples proceeds as follows:

7.6.1 **Impinger and organic module thermocouples:** For the thermocouples used to measure the temperature of the gas leaving the impinger train and the XAD-2 resin bed, a three-point calibration at ice water, room-air, and boiling-water temperatures is necessary. Accept the thermocouples only if the readings at all three temperatures agree within 2°C (3.6°F) of the absolute value of the reference thermometer.

7.6.2 **Dry-gas-meter thermocouples:** For the thermocouples used to indicate the dry-gas-meter inlet and outlet temperatures, a three-point calibration at ice-water, room-air, and boiling-water temperatures must be performed. The values must be within 2°C (3.6°F) of the absolute reference thermometer value at all three calibration points.

7.6.3 **Probe and stack thermocouple:** For the thermocouples used to indicate the probe and stack temperatures, a three-point calibration at ice-water, boiling-water, and boiling cooking-oil temperatures must be performed; it is highly recommended that room-air temperature be added as a fourth calibration point. If the absolute values of the reference thermometer and the thermocouple agree within 1.5% at each of the calibration points, a calibration curve (equation) may be constructed (calculated), and the data extrapolated to cover the entire temperature range suggested by the manufacturer.

7.7 Barometer: Adjust the field barometer initially and before each test series to agree within 2.5 mm Hg (0.1 in. Hg) of the mercury barometer, or within the station barometric pressure value reported by a nearby National Weather Service station and corrected for elevation.

7.8 Triple-Beam Balance: Calibrate the triple beam balance before each test series using Class-S standard weights; the weights must be within 0.5 g of the standards, or the balance adjusted to meet these limits.

7.9 Analytical Balance: Calibrate the analytical balance with Class-S weights before initially tare-weighing each set of filters. The balance must agree or be adjusted to within 2 mg of the standards. Run at least one standard each time one or more of the filters is reweighed.

8.0 CALCULATIONS

8.1 Dry gas volume:

8.1.1 From the SASS run sheet, average the dry-gas-meter temperatures and orifice pressure drops readings throughout the run. Calculate the Volume of Dry Gas Sampled at standard conditions (20°C, 760 mm Hg [528°R, 29.92 in. Hg]) using the equation:

$$V_{m(std)} = V_m \gamma \frac{(T_{std})}{T_m} \frac{(P_{bar} + (\Delta H/13.6))}{P_{std}}$$

$$= K_1 V_m \gamma \frac{(P_{bar} + (\Delta H/13.6))}{T_m}$$

where:

$V_{m(std)}$ = Volume of dry gas sampled at standard conditions, dscm (dscf);

V_m = Volume of dry gas sampled at dry-gas-meter conditions, dcm (dcf);

γ = Dry-gas-meter calibration factor, dimensionless;

T_m = Average dry-gas-meter temperature, °K (°R);

T_{std} = Standard absolute temperature, °K (°R);

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg);

P_{std} = Standard absolute pressure, mm Hg (in. Hg);

ΔH = Average orifice pressure drop during the sampling run, mm H_2O (in. H_2O); and

K_1 = 0.358°K/mm for metric units
= 17.64°R/in. Hg for English units.

8.1.2 The above equation must be modified whenever the leakage rate observed during any of the mandatory leak-checks (i.e., the post-test leak-checks or leak-checks made prior to component changes) exceeds the maximum allowed. The modification follows:

8.1.2.1 Case I (No component changes have been made during the sampling run, and the allowable leakage rate has been exceeded during the post-test leak-check): Replace V_m with the expression:

$$V_m - [(L_p - L_a)\theta]$$

where:

L_p = Leakage rate observed during post-test leak-check, m^3/min (cfm);

L_a = Maximum allowed leakage rate, 0.0014 m^3/min (0.05 ft^3/min); and

θ = Total sampling time, min.

8.1.2.2 Case II (One or more component changes made during the sampling run, and the allowable leakage rate has been exceeded

during one or more of the leak-checks prior to component changes or during the post-test leak-check): Replace V_m with the expression:

$$V_m - \sum_{i=1}^{n} \left[\theta_{i-1}(L_i - L_a) - \theta_p(L_p - L_a) \right]$$

where:

L_i = Leakage rate observed prior to "i^{th}" component change if the allowable leakage rate has been exceeded while sampling with the "i^{th}" component, m^3/min (cfm);

L_a = Maximum allowed leakage rate, 0.0014 m^3/min (0.05 ft^3/min);

θ_{i-1} = Sampling time interval between the successive component changes in which the allowable leakage rate has been exceeded, min;

L_p = Leakage rate observed during post-test leak-check, if the allowable leakage rate has been exceeded, m^3/min (cfm); and

θ_p = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, if the allowable leakage rate has been exceeded during the post-test leak-check, min.

8.2 Moisture content:

8.2.1 Calculate the Volume of Water Vapor at standard conditions:

$$V_{w(std)} = \left[\frac{\rho_w}{M_w} \right] \left[\frac{RT_{std}}{P_{std}} \right] = K_2 V_{lc}$$

where:

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, dscm (dscf);

V_{lc} = Volume of liquid collected in the condensate reservoir added to the net increase in impinger solution volumes and silica gel weight gain during the run, mL;

ρ_w = Density of water, 0.9982 g/mL (0.002201 lb/mL);

M_w = Molecular weight of water, 18.0 g/g-mole (lb/lb-mole);

R = Ideal gas constant, 0.06236 mm Hg-m^3/°K-g-mole (21.85 in. Hg-ft^3/°R-lb-mole);

T_{std} = Standard absolute temperature, °K (°R);

P_{std} = Standard absolute pressure, mm Hg (in. Hg); and

K_2 = 0.001333 m^3/mL for metric units
= 0.04707 ft^3/mL for English units.

8.2.2 Calculate the Stack Gas Moisture Content (equal to B_{ws} x 100 for conversion to percent):

$$\%M = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} = B_{ws} \times 100$$

where:

B_{ws} = Proportion of water vapor in the gas stream by volume, dimensionless;

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, dscm (dscf); and

$V_{m(std)}$ = Volume of gas measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

8.2.3 In saturated or water-droplet-laden gas streams, make two calculations of the moisture content, one from the total volume of liquid collected in the train and one from the assumption of saturated gas-stream conditions. Use whichever method results in the lower value. To determine the moisture content based upon saturated conditions, use the average stack gas temperature in conjunction with: (1) a psychrometric chart, correcting for difference between the chart and the absolute stack pressure; or (2) saturation vapor pressure tables.

8.3 Particulate concentration:

8.3.1 Calculate the Unit Methanol/Methylene Chloride Blank Correction for all front-half samples:

$$C_{mm} = \frac{M_{mm}}{V_{mm}\rho_{mm}}$$

where:

C_{mm} = Methanol/methylene chloride blank correction, mg/g;

M_{mm} = Mass of methanol/methylene chloride after evaporation, mg;

V_{mm} = Volume of methanol/methylene chloride used in wash, mL; and

ρ_{mm} = Density of 50:50 mix of methanol/methylene chloride, mg/mL (see labels on bottles).

8.3.2 Calculate the Total Methanol/Methylene Chloride Blank Weight Correction for each individual front-half sample:

$$W_{mm} = C_{mm} V_{mm} \rho_{mm}$$

where:

W_{mm} = Weight of residue in methanol/methylene chloride front-half wash, mg;

C_{mm} = Methanol/methylene chloride unit blank correction, mg/g;

V_{mm} = Volume of methanol/methylene chloride used for front-half wash, mL; and

ρ_{mm} = Density of 50:50 mixture of methanol and methylene chloride, mg/mL.

8.3.3 Calculate Total Particulate Weight:

$$W_p = (W_{pf-a} + W_{pf-b} + \ldots\ldots) + (W_{10c} + W_{3c} + W_{1c}) + (W_{pr} - W_{mm})$$

where:

W_p = Total particulate weight, mg;

$W_{pf-a+\ldots}$ = Particulate weight from filter Pf-a + Pf-b + ... ;

W_{10c}, W_{3c}, W_{1c} = Particulate weight catch from the 10-, 3-, and 1-um cyclones, respectively, mg;

W_{pr} = Weight of front-half rinse residue before blank correction, mg; and

W_{mm} = Methanol/methylene chloride blank weight correction, mg.

8.3.4 Calculate the Total Particulate Concentration:

$$C_p = (0.001\ g/mg)\ (W_p/V_{m(std)})$$

where:

C_p = Concentration of particulate material in the stack gas, g/dscm (gr/dscf);

W_p = Weight of particulate material collected during run, mg; and

$V_{m(std)}$ = Volume of gas sampled, dscm (dscf).

8.3.5 To convert the above concentration to units of gr/ft^3 or lb/ft^3 for comparison with established or projected values, the following conversion factors are useful:

From:	To:	Multiply By:
scf	m^3	0.02832
g/ft^3	gr/ft^3	15.43
g/ft^3	lb/ft	2.205×10^{-3}
g/ft^3	g/m^3	35.315

8.4 Concentration of organic material:

8.4.1 Calculate the Volumetric Flow Rate (Q_{sd}) during the run. Determine the average stack gas velocity and volumetric flow rate from actual run data in the same manner that these were calculated during preliminary determinations (see Paragraph 4.3).

8.4.2 Calculate the POHC Concentration:

$$C_{pohc} = \frac{M_{pohc}}{Q_{sd}} = \frac{M_{cd\text{-}le} + M_{mrx}}{Q_{sd}}$$

where:

C_{pohc} = Concentration of POHCs in stack gas, ug/dscm;

M_{pohc} = Total mass of POHCs collected in XAD-2 and organic module rinse, and in the condensate extract, ug;

$M_{cd\text{-}le}$ = Mass of POHCs extracted from the condensate (corrected for methylene chloride blank extraction residue), ug;

M_{mrx} = Mass of POHCs extracted from the XAD-2 sorbent and organic module rinse (corrected for methylene chloride blank extraction residue), ug; and

Q_{sd} = Volumetric flow rate during the run, dscm.

8.5 Isokinetic variation:

8.5.1 Having calculated T_s, $V_{m(std)}$, V_s, A_n, P_s, and B_{ws}, determine the Isokinetic Variation using the equation:

$$I = K_4 \frac{T_s V_{m(std)}}{P_s V_s A_n \theta (1-B_{ws})}$$

where:

I = Isokinetic variation, %;

T_s = Absolute average stack gas temperature, °K (°R);

$V_{m(std)}$ = Volume of gas sampled, dscm (dscf);

P_s = Absolute stack gas pressure, mm Hg (in. Hg);

V_s = Stack gas velocity, m/sec (ft/sec);

A_n = Cross-sectional area of nozzle, m^3 (ft^3);

θ = Net sampling time, min;

B_{ws} = Proportion of water vapor in gas stream by volume, dimensionless; and

K_4 = 4.320 for metric units
= 0.09450 for English units.

8.5.2 For the accuracy of Level 1 requirements (factor of 3) for measured particulate emissions, the isokinetic variation must be within 70-150%.

8.6 Cyclone particle-size cutoff diameter:

8.6.1 The particle-size cutoff diameter represents that particle diameter (assuming spherical particles of unit density) at which the cyclone exhibits 50% collection efficiency; it is expressed as the "d_{50}." The range of particle size collected in each cyclone and on the filter is dependent upon the operating temperature and flow rate through each of

these components. The particle-size cutoff diameters of 10, 3, and 1 um in the cyclones are the result of calibration of these at 400°F and 4.0 scfm (6.5 acfm). When the determined isokinetic sampling rate is not 4.0 scfm, or when it is necessary to maintain a constant subisokinetic sampling rate (still within the limits of Level 1 accuracy) during the SASS run, the particle-size cutoff diameters for the cyclones must be extrapolated.

8.6.2 Existing calibration data is insufficient to determine exact mathematical relationships for variations of particle-size cutoff diameter with temperature and with volumetric flow rate. The best estimates (McCain, 1983) suggest that a square, and an inverse square root dependence, respectively, exist; the extrapolation equation is presented below.

8.6.2.1 Calculate the Gas Viscosity from the equation:

$$\mu = (1.68 \times 10^{-4}) + (2.292 \times 10^{-7})\ (T)$$

where:

μ = Gas viscosity, poise; and

T = Gas temperature, °F.

8.6.2.2 Extrapolate the Particle Size Cutoff Diameter from:

$$D_{T_a,F_a} = D_{400,4.0} \frac{\left[\frac{\mu_{400}}{\mu_{T_a}}\right]^2}{\left[\frac{V_{4.0}}{V_{F_a}}\right]^{1/2}} = D_{400,4.0} \frac{3.37\sqrt{V_{F_a}}}{\mu^2 T_a}$$

where:

D_{T_a,F_a} = Particle size cutoff diameter at cyclone operating a temperature and flow rate, um (note that the volumetric flow rate must be corrected to standard conditions);

$D_{400,4.0}$ = Particle size cutoff diameter at an operating temperature of 400°F and flow rate of 4.0 scfm, um;

μ_{400} = Gas viscosity at 400°F, poise;

μT_a = Gas viscosity at operating conditions, poise;

$V_{4.0}$ = Cyclone volumetric flow rate of 4.0 scfm; and

V_{F_a} = Cyclone volumetric flow rate at operating conditions, scfm.

This equation reduces to:

1. $\dfrac{33.7\sqrt{V_{F_a}}}{\mu T_a^2}$ for the 10-um cyclone,

2. $\dfrac{10.1\sqrt{V_{F_a}}}{\mu T_a^2}$ for the 3-um cyclone,

3. $\dfrac{3.37\sqrt{V_{V_a}}}{\mu T_a^2}$ for the 1-um cyclone,

8.7 Cumulative particulate weight percent less than calculated size:

8.7.1 Divide the weight collected in the individual cyclones and on the filter by the total weight of particulate collected; express these as a percentage, using the following equations:

$$\% W_{pf} = \frac{W_{pf\text{-}a} + W_{pf\text{-}b} + \ldots}{W_p} \times 100$$

$$\% W_{10c} = \frac{W_{10c}}{W_p} \times 100$$

$$\% W_{3c} = \frac{W_{3c}}{W_p} \times 100$$

$$\% W_{1c} = \frac{W_{1c}}{W_p} \times 100$$

where:

W_p = Total particulate weight collected, mg;

W_{pf} = $W_{pf\text{-}a} + W_{pf\text{-}b} + \ldots$

= Particulate weight collected on filters PF-a + PF-b, etc., mg;

W_{10c} = Particulate weight collected in 10-um cyclone, mg;

W_{3c} = Particulate weight collected in 3-um cyclone, mg;

W_{1c} = Particulate weight collected in 1-um cyclone, mg; and

100 = Conversion to percent.

8.7.2 Calculate the Cumulative Weight Percent Less than the Calculated Particle Size Cutoff Diameter by adding, to each weight percent, the weight percent of all fractions having a smaller particle-size cutoff diameter. Tabulate the data, using the form below as an example:

PRESENTATION OF SASS PARTICLE SIZING DATA

Stage	Weight % Collected in Stage	Cumulative Weight % Less than Calculated Particle Size Cutoff Diameter	Calculated Particle Size Cutoff Diameter
10-um cyclone			
3-um cyclone			
1-um cyclone			
Glass fiber filter			

9.0 REFERENCES

9.1 References

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METHOD 0030

VOLATILE ORGANIC SAMPLING TRAIN

1.0 PRINCIPLE AND APPLICATION

1.1 Principle

1.1.1 This method describes the collection of volatile principal organic hazardous constituents (POHCs) from the stack gas effluents of hazardous waste incinerators. For the purpose of definition, volatile POHCs are those POHCs with boiling points less than 100°C. If the boiling point of a POHC of interest is less than 30°C, the POHC may break through the sorbent under the conditions of the sample collection procedure.

1.1.2 Field application for POHCs of this type should be supported by laboratory data which demonstrate the efficiency of a volatile organic sampling train (VOST) to collect POHCs with boiling points less than 30°C. This may require using reduced sample volumes collected at flow rates between 250 and 500 mL/min. Many compounds which boil above 100°C (e.g., chlorobenzene) may also be efficiently collected and analyzed using this method. VOST collection efficiency for these compounds should be demonstrated, where necessary, by laboratory data of the type described above.

1.1.3 This method employs a 20-liter sample of effluent gas containing volatile POHCs which is withdrawn from a gaseous effluent source at a flow rate of 1 L/min, using a glass-lined probe and a volatile organic sampling train (VOST). (Operation of the VOST under these conditions has been called FAST-VOST.) The gas stream is cooled to 20°C by passage through a water-cooled condenser and volatile POHCs are collected on a pair of sorbent resin traps. Liquid condensate is collected in an impinger placed between the two resin traps. The first resin trap (front trap) contains approximately 1.6 g Tenax and the second trap (back trap) contains approximately 1 g each of Tenax and petroleum-based charcoal (SKC Lot 104 or equivalent), 3:1 by volume. A total of six pairs of sorbent traps may be used to collect volatile POHCs from the effluent gas stream.

1.1.4 An alternative set of conditions for sample collection has been used. This method involves collecting sample volume of 20 liters or less at reduced flow rate. (Operation of the VOST under these conditions has been referred to as SLO-VOST.) This method has been used to collect 5 liters of sample (0.25 L/min for 20 min) or 20 liters of sample (0.5 L/min for 40 min) on each pair of sorbent cartridges. Smaller sample volumes collected at lower flow rates should be considered when the boiling points of the POHCs of interest are below 35°C. A total of six pairs of sorbent traps may be used to collect volatile POHCs from the effluent gas stream.

1.1.5 Analysis of the traps is carried out by thermal desorption purge-and-trap by gas chromatography/mass spectrometry (see Method 5040). The VOST is designed to be operated at 1 L/min with traps being replaced every 20 min for a total sampling time of 2 hr. Traps may be analyzed separately or combined onto one trap to improve detection limit. However, additional flow rates and sampling times are acceptable. Recent experience has shown that when less than maximum detection ability is required, it is acceptable and probably preferable to operate the VOST at 0.5 L/min for a total of three 40-min periods. This preserves the 2-hr sampling period, but reduces the number of cartridge changes in the field as well as the number of analyses required.

1.2 Application

1.2.1 This method is applicable to the determination of volatile POHCs in the stack gas effluent of hazardous waste incinerators. This method is designed for use in calculating destruction and removal efficiency (DRE) for the volatile POHCs and to enable a determination that DRE values for removal of the volatile POHCs are equal to or greater than 99.99%.

1.2.2 The sensitivity of this method is dependent upon the level of interferences in the sample and the presence of detectable levels of volatile POHCs in blanks. The target detection limit of this method is 0.1 ug/m^3 (ng/L) of flue gas, to permit calculation of a DRE equal to or greater than 99.99% for volatile POHCs which may be present in the waste stream at 100 ppm. The upper end of the range of applicability of this method is limited by breakthrough of the volatile POHCs on the sorbent traps used to collect the sample. Laboratory development data have demonstrated a range of 0.1 to 100 ug/m^3 (ng/L) for selected volatile POHCs collected on a pair of sorbent traps using a total sample volume of 20 liters or less (see Paragraph 1.1.4).

1.2.3 This method is recommended for use only by experienced sampling personnel and analytical chemists or under close supervision by such qualified persons.

1.2.4 Interferences arise primarily from background contamination of sorbent traps prior to or after use in sample collection. Many potential interferences can be due to exposure of the sorbent materials to solvent vapors prior to assembly and exposure to significant concentrations of volatile POHCs in the ambient air at hazardous waste incinerator sites.

1.2.5 To avoid or minimize the low-level contamination of train components with volatile POHCs, care should be taken to avoid contact of all interior surface or train components with synthetic organic materials (e.g., organic solvents, lubricating and sealing greases), and train components should be carefully cleaned and conditioned according to the procedures described in this protocol.

2.0 APPARATUS

2.1 Volatile Organic Sampling Train: A schematic diagram of the principal components of the VOST is shown in Figure 1 and a diagram of one acceptable version of the VOST is shown in Figure 2. The VOST consists of a glass-lined probe followed by an isolation valve, a water-cooled glass condenser, a sorbent cartridge containing Tenax (1.6 g), an empty impinger for condensate removal, a second water-cooled glass condenser, a second sorbent cartridge containing Tenax and petroleum-based charcoal (3:1 by volume; approximately 1 g of each), a silica gel drying tube, a calibrated rotameter, a sampling pump, and a dry gas meter. The gas pressure during sampling and for leak-checking is monitored by pressure gauges which are in line and downstream of the silica gel drying tube. The components of the sampling train are described below.

2.1.1 **Probe:** The probe should be made of stainless steel with a borosilicate or quartz glass liner. The temperature of the probe is to be maintained above 130°C but low enough to ensure a resin temperature of 20°C. A water-cooled probe may be required at elevated stack temperatures to protect the probe and meet the above requirements. Isokinetic sample collection is not a requirement for the use of VOST since the compounds of interest are in the vapor phase at the point of sample collection.

2.1.2 **Isolation valve:** The isolation valve should be a greaseless stopcock with a glass bore and sliding Teflon plug with Teflon wipers (Ace 8193 or equivalent).

2.1.3 **Condensers:** The condensers (Ace 5979-14 or equivalent) should be of sufficient capacity to cool the gas stream to 20°C or less prior to passage through the first sorbent cartridge. The top connection of the condenser should be able to form a leak-free, vacuum-tight seal without using sealing greases.

2.1.4 **Sorbent cartridges:**

2.1.4.1 The sorbent cartridges used for the VOST may be used in either of two configurations: the inside-outside (I/O) configuration in which the cartridge is held within an outer glass tube and in a metal carrier, and the inside-inside (I/I) configuration in which only a single glass tube is used, with or without a metal carrier. In either case, the sorbent packing will be the same.

2.1.4.1.1 The first of a pair of sorbent cartridges shall be packed with approximately 1.6 g Tenax GC resin and the second cartridge of a pair shall be packed with Tenax GC and petroleum-based charcoal (3:1 by volume; approximately 1 g of each).

2.1.4.1.2 The second sorbent cartridge shall be packed so that the sample gas stream passes through the Tenax layer first and then through the charcoal layer.

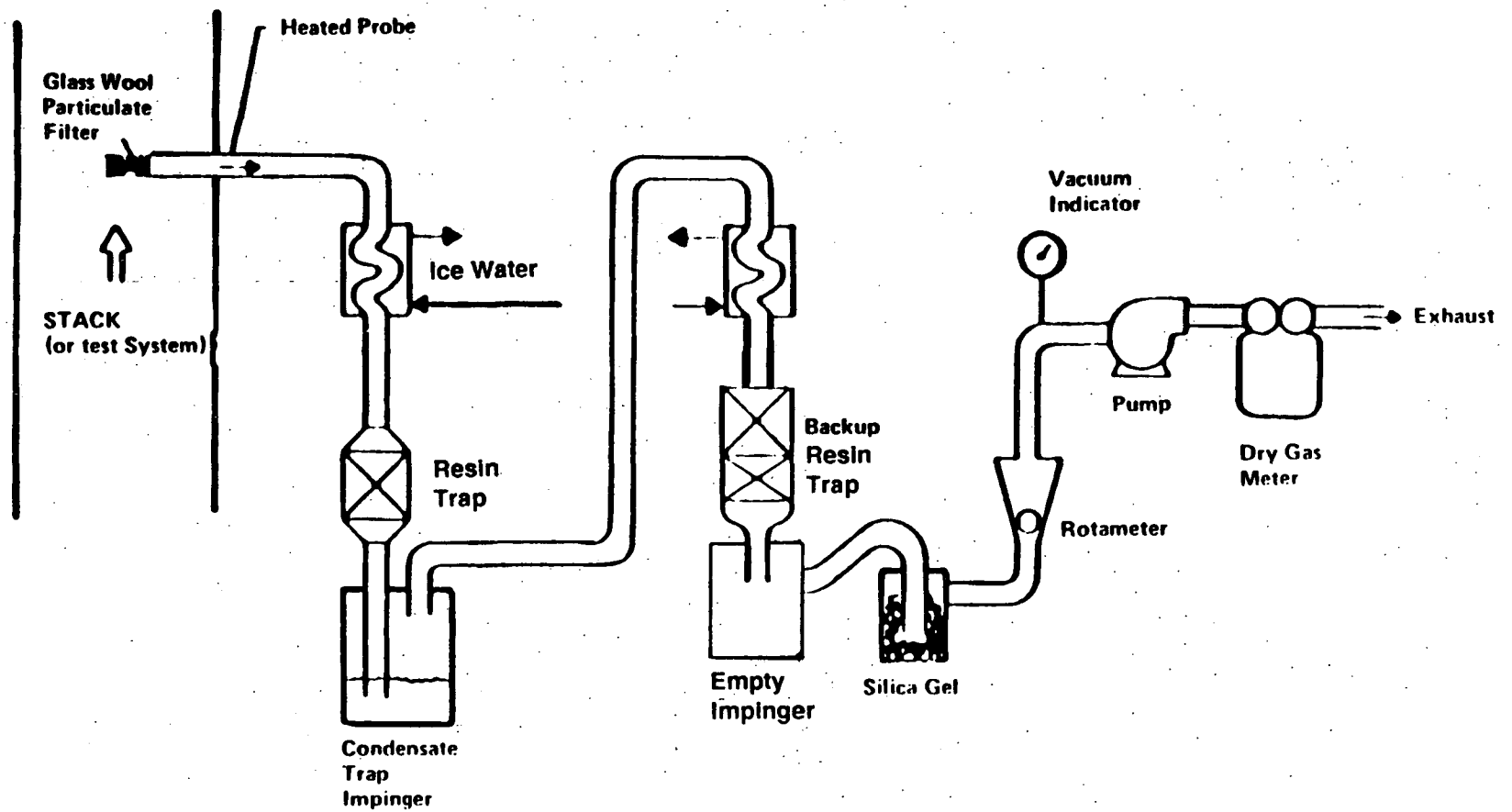


Figure 1. Schematic of Volatile Organic Sampling Train (VOST).

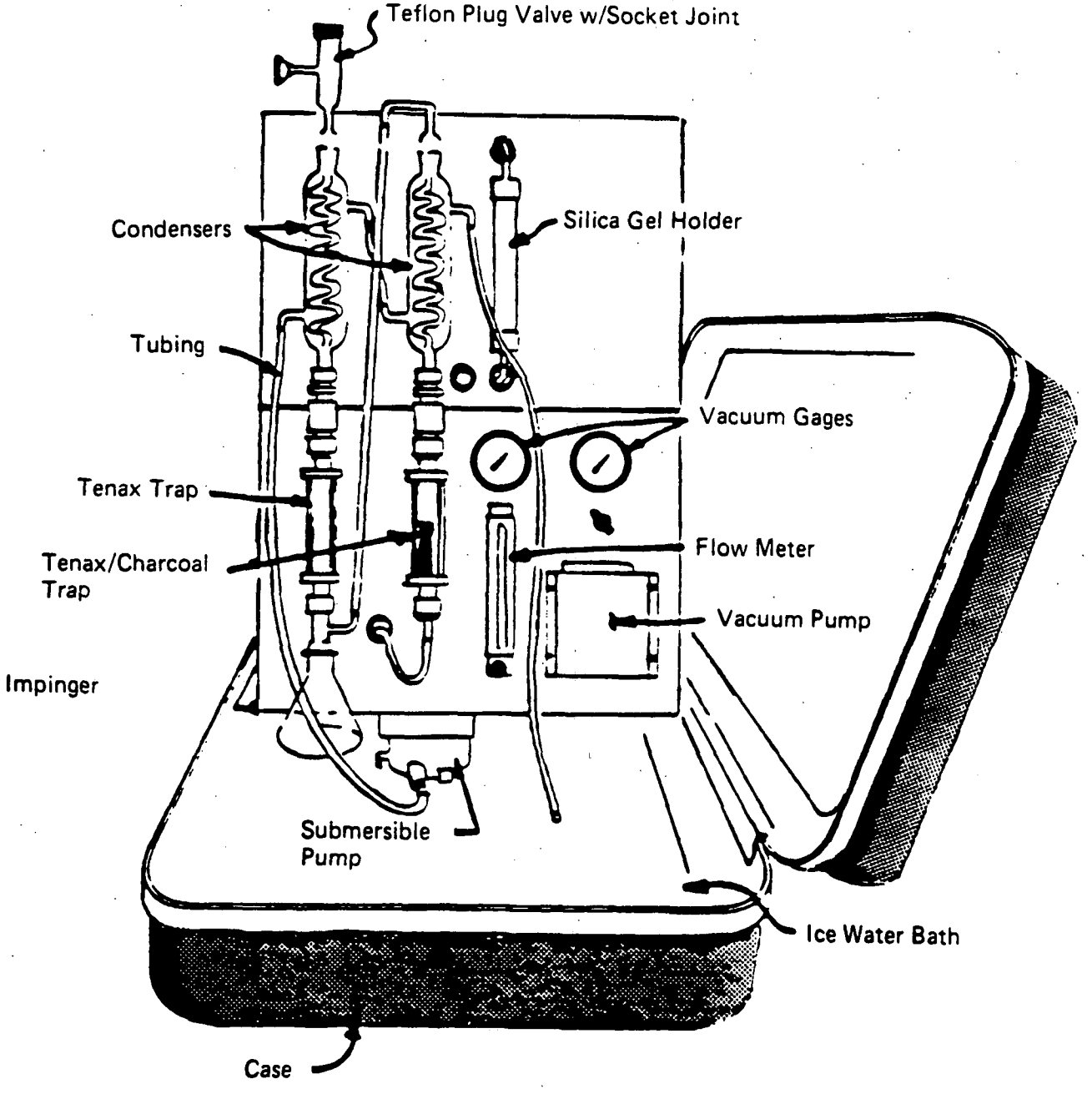


Figure 2. Volatile Organic Sampling Train (VOST).

2.1.4.2 The sorbent cartridges shall be glass tubes with approximate dimensions of 10 cm by 1.6 cm I.D. The two acceptable designs (I/O, I/I) for the sorbent cartridge are described in further detail below.

2.1.4.2.1 **Inside/Inside sorbent cartridge:** A diagram of an I/I sorbent cartridge is shown in Figure 3. This cartridge is a single glass tube (10 cm by 1.6 cm I.D.) which has the ends reduced in size to accommodate a 1/4- or 3/8-in. Swagelok or Cajon gas fitting. The resin is held in place by glass wool at each end of the resin layer. The amounts of each type of sorbent material used in the I/I design are the same as for the I/O design. Threaded end caps are placed on the sorbent cartridge after packing with sorbent to protect the sorbent from contamination during storage and transport.

2.1.4.2.2 **Inside/Outside type sorbent cartridge:** A diagram of an I/O sorbent cartridge is shown in Figure 4. In this design the sorbent materials are held in the glass tube with a fine mesh stainless steel screen and a C-clip. The glass tube is then placed within a larger diameter glass tube and held in place using Viton O-rings. The purpose of the outer glass tube is to protect the exterior of the resin-containing tube from contamination. The two glass tubes are held in a stainless steel cartridge holder, where the ends of the glass tubes are held in place by Viton O-rings placed in machine grooves in each metal end piece. The three cylindrical rods are secured in one of the metal end pieces and fastened to the other end piece using knurled nuts, thus sealing the glass tubes into the cartridge holder. The end pieces are fitted with a threaded nut onto which a threaded end cap is fitted with a Viton O-ring seal, to protect the resin from contamination during transport and storage.

2.1.5 **Metering system:** The metering system for VOST shall consist of vacuum gauges, a leak-free pump (Thomas Model 107 or equivalent, Thomas Industries, Sheboygan, Wisconsin), a calibrated rotameter (Linde Model 150, Linde Division of Union Carbide, Keasbey, New Jersey) for monitoring the gas flow rate, a dry gas meter with 2% accuracy at the required sampling rate, and related valves and equipment. Provisions should be made for monitoring the temperature of the sample gas stream between the first condenser and first sorbent cartridge. This can be done by placing a thermocouple on the exterior glass surface of the outlet from the first condenser. The temperature at that point should be less than 20°C. If it is not, an alternative condenser providing the required cooling capacity must be used.

2.1.6 **Sample transfer lines:** All sample transfer lines to connect the probe to the VOST shall be less than 5 ft in length, and shall be heat-traced Teflon with connecting fittings which are capable of forming leak-free, vacuum-tight connections without the use of sealing grease.

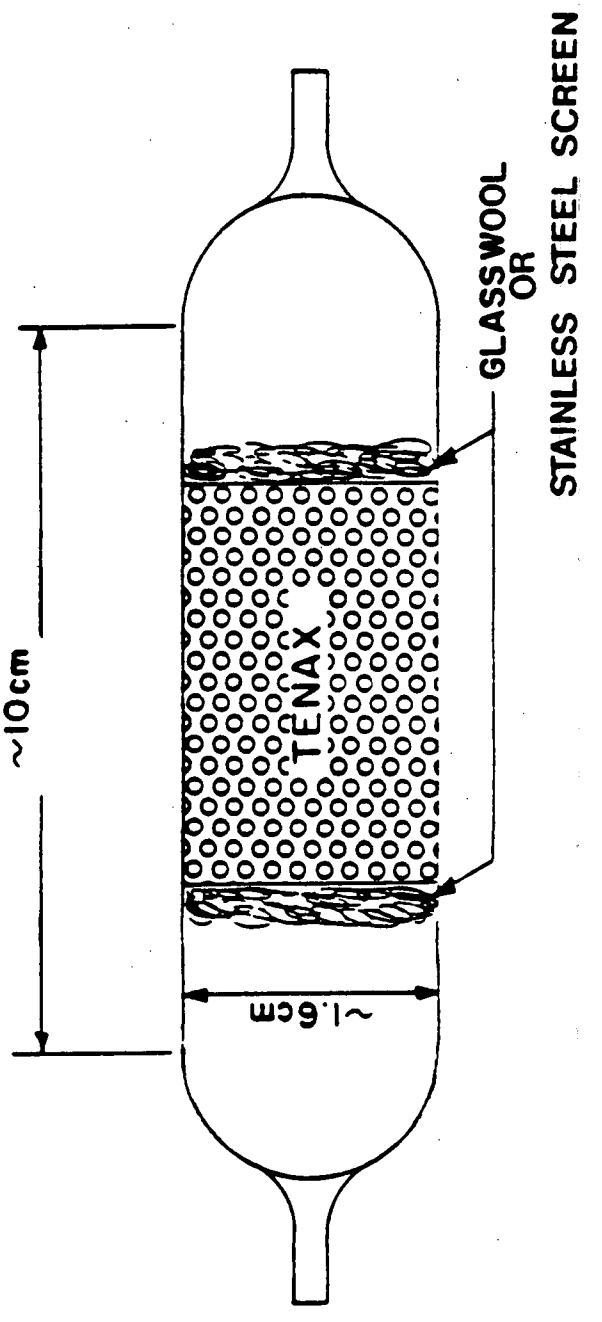
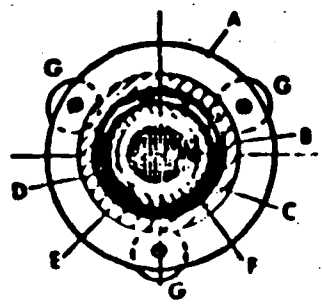


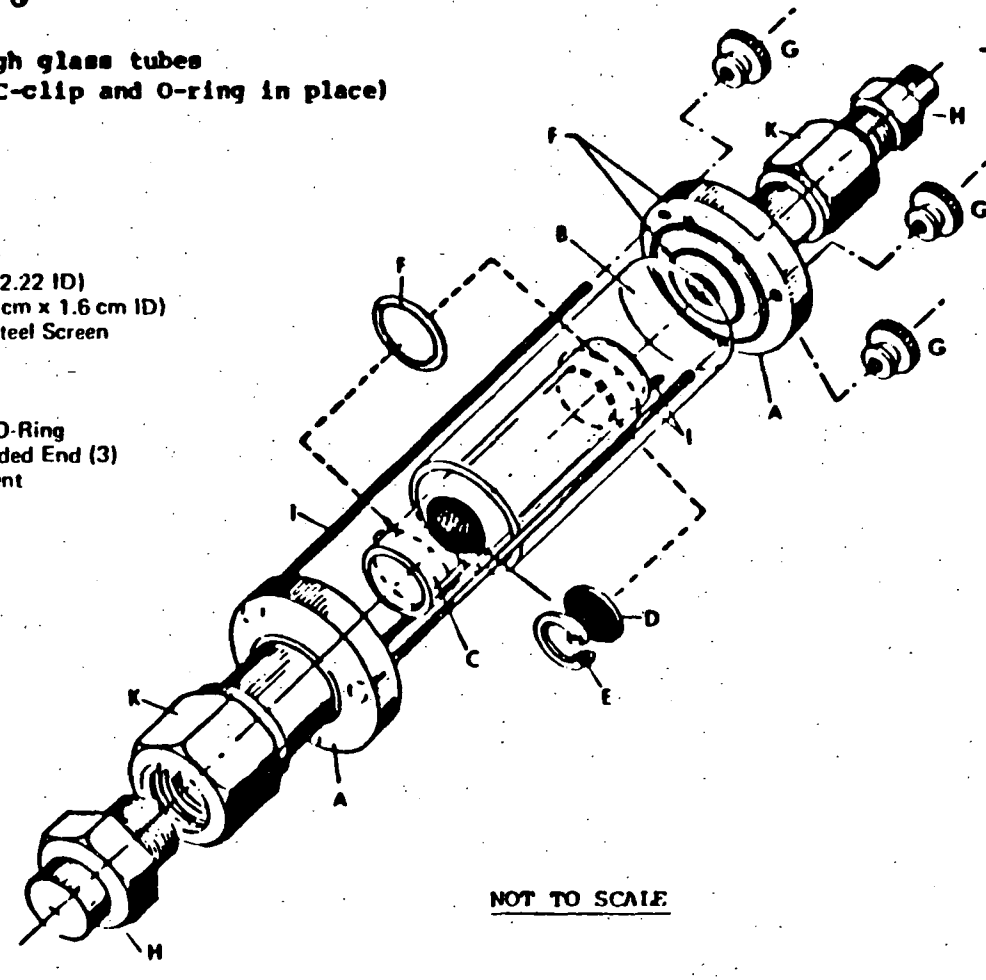
Figure 3. Inside-inside vost cartridge



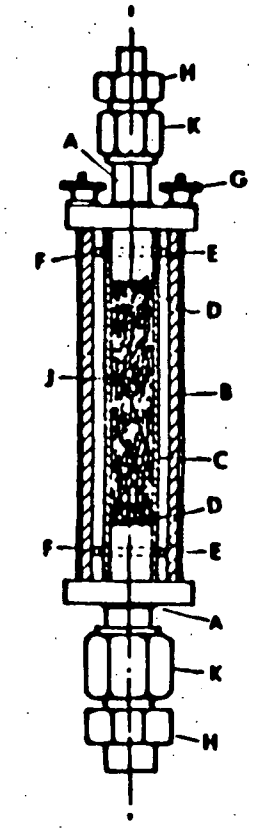
Section cut through glass tubes
(showing screen, C-clip and O-ring in place)

LEGEND

A - Stainless Steel Carrier
B - Glass Tube (9.84 L x 2.22 ID)
C - Small Glass Tube (10 cm x 1.6 cm ID)
D - Fine Mesh Stainless Steel Screen
E - Stainless Steel C-Clip
F - O-Ring (Viton)
G - Nuts (+)
H - End Cap with Viton O-Ring
I - Metal Rod with Threaded End (3)
J - Tenax/Charcoal Sorbent
K - Cajon Fitting



NOT TO SCALE



Assembled Trap
NTS

Figure 4. Sorbent Trap Assembly (I/O)
Volatile Organic Sampling Train (VOST)

Revision 0
Date September 1986

All other sample transfer lines used with the VOST shall be Teflon with connecting fittings that are capable of forming leak-free, vacuum-tight connections without the use of sealing grease.

3.0 REAGENTS AND MATERIALS

3.1 2,6-Diphenylene oxide polymer (Tenax, 35/60 mesh):

3.1.1 The new Tenax is Soxhlet extracted for 24 hr with methanol (Burdick & Jackson, pesticide grade or equivalent). The Tenax is dried for 6 hr in a vacuum oven at 50°C before use. Users of I/O and I/I sorbent cartridges have used slightly different thermal conditioning procedures. I/O sorbent cartridges packed with Tenax are thermally conditioned by flowing organic-free nitrogen (30 mL/min) through the resin while heating to 190°C. Some users have extracted new Tenax and charcoal with pentane to remove nonpolar impurities. However, these users have experienced problems with residual pentane in the sorbents during analysis.

3.1.2 If very high concentrations of volatile POHCs have been collected on the resin (e.g., micrograms of analytes), the sorbent may require Soxhlet extraction as described above. Previously used Tenax cartridges are thermally reconditioned by the method described above.

3.2 Charcoal (SKC petroleum-base or equivalent): New charcoal is prepared and charcoal is reconditioned as described in Paragraph 4.4. New charcoal does not require treatment prior to assembly into sorbent cartridges. Users of VOST have restricted the types of charcoal used in sorbent cartridges to only petroleum-based types. Criteria for other types of charcoal are acceptable if recovery of POHC in laboratory evaluations meet the criteria of 50 to 150%.

3.3 Viton-O-Ring: All O-rings used in VOST shall be Viton. Prior to use, these O-rings should be thermally conditioned at 200°C for 48 hr. O-rings should be stored in clean, screw-capped glass containers prior to use.

3.4 Glass tubes/Condensers: The glass resin tubes and condensers should be cleaned with a nonionic detergent in an ultrasonic bath, rinsed well with organic-free water, and dried at 110°C. Resin tubes of the I/O design should be assembled prior to storage as described in Paragraph 4.1. Resin tubes of the I/I design can be stored in glass culture tube containers with cotton cushioning and Teflon-lined screw caps. Condensers can be capped with appropriate end caps prior to use.

3.5 Metal parts: The stainless steel carriers, C-clips, end plugs, and screens used in the I/O VOST design are cleaned by ultrasonication in a warm nonionic detergent solution, rinsed with distilled water, air-dried, and heated in a muffle furnace for 2 hr at 400°C. Resin tubes of the I/I design require Swagelok or equivalent end caps with Supelco M-1 ferrules. These should be heated at 190°C along with the assembled cartridges.

3.6 Silica gel (Indicating type, 6-16 mesh): New silica gel may be used as received. Silica gel which has been previously used should be dried for 2 hr at 175°C (350°F).

3.7 Cold packs: Any commercially available reusable liquids or gels that can be repeatedly frozen are acceptable. They are typically sold in plastic containers as "Blue Ice" or "Ice-Packs." Enough should be used to keep cartridges at or near 4°C.

3.8 Water: Water used for cooling train components in the field may be tap water; and water used for rinsing glassware should be organic-free.

3.9 Glass wool: Glass wool should be Soxhlet extracted for 8 to 16 hr, using methanol, and oven dried at 110°C before use.

4.0 SAMPLE HANDLING AND PROCEDURE

4.1 Assembly:

4.1.1 The assembly and packing of the sorbent cartridges should be carried out in an area free of volatile organic material, preferably a laboratory in which no organic solvents are handled or stored and in which the laboratory air is charcoal filtered. Alternatively, the assembly procedures can be conducted in a glove box which can be purged with organic-free nitrogen.

4.2 Tenax cartridges:

4.2.1 The Tenax, glass tubes, and metal cartridge parts are cleaned and stored (see Section 3.0). Approximately 1.6 g of Tenax is weighed and packed into the sorbent tube which has a stainless steel screen and C-clip (I/O design) or glass wool (I/I design) in the downstream end. The Tenax is held in place by inserting a stainless steel screen and C-clips in the upstream end (I/O design) or glass wool (I/I design). Each cartridge should be marked, using an engraving tool, with an arrow to indicate the direction of sample flow, and a serial number.

4.2.2 Conditioned resin tubes of the I/O design are then assembled into the metal carriers according to the previously described inside/inside or inside/outside procedures (with end caps) and are placed on cold packs for storage and transport. Conditioned resin tubes of the I/I design are capped and placed on cold packs for storage and transport.

4.3 Tenax/Charcoal tubes

4.3.1 The Tenax, charcoal, and metal cartridge parts are cleaned and stored as previously described (see Section 3.0). The tubes are packed with approximately a 3:1 volume ratio of Tenax and charcoal (approximately 1 g each). The Tenax and charcoal are held in place by the stainless steel screens and C-clips (I/O design) or by glass wool (I/I design). The glass tubes containing the Tenax and charcoal are then

conditioned as described below (see Paragraph 4.4). Place the I/O glass tubes in the metal carriers (see Paragraph 2.1.4.2.2), put end caps on the assembled cartridges, mark direction of sample flow and serial number, and place the assembled cartridges on cold packs for storage and transport.

4.3.2 Glass tubes of the I/I design are conditioned, and stored in the same manner as the I/O tubes.

4.4 Trap Conditioning - QC

4.4.1 Following assembly and leak-checking, the traps are connected in reverse direction to sampling to a source of organic-free nitrogen, and nitrogen is passed through each trap at a flow rate of 40 mL/min, while the traps are heated to 190°C for 12-28 hr. The actual conditioning period may be determined based on adequacy of the resulting blank checks.

4.4.2 The following procedure is used to blank check each set of sampling cartridges prior to sampling to ensure cleanliness. The procedure provides semi-quantitative data for organic compounds with boiling points below 110°C on Tenax and Tenax/Charcoal cartridges. It is not intended as a substitute for Method 5040.

4.4.2.1 The procedure is based on thermal desorption of each set of two cartridges, cryofocusing with liquid nitrogen onto a trap packed with glass beads, followed by thermal desorption from the trap and analysis by GC/FID.

4.4.2.2 The detection limit is based on the analysis of Tenax cartridges spiked with benzene and toluene and is around 2 ng for each compound.

4.4.2.3 The results of analyzing spiked cartridges on a daily basis should not vary by more than 20 percent. If the results are outside this range, the analytical system must be evaluated for the probable cause and a second spiked cartridge analyzed.

4.4.2.4 The GC operating conditions are as follows:

GC Operating Conditions

Column: Packed column 6 ft x 1/8" stainless steel 1.0 percent SP-1000 on Carbopack B 60/80, or equivalent.
Temperature program: 50°C for 5 min, 20°C/min increase to 190°C, hold 13 min.
Injector: 200°C.
Detector: F.I.D. 250°C.
Carrier Gas: Helium at 25 mL/min.
Sample valve: Valco 6-port with 40" x 1/16" stainless steel trap packed with 60/80 mesh glass beads.
Cryogen: Liquid nitrogen.
Trap heater: Boiling water, hot oil, or electrically heated.

Desorption heater: Supelco "clam shell" (high capacity carrier gas purifier) heater and Variac, adjusted to 180°C to 200°C.

4.4.2.5 Calibration is accomplished by preparing a spiked Tenax cartridge with benzene and toluene and analyzing according to the standard operating procedure. A standard of benzene, toluene and bromofluorobenzene (BFB) is prepared by injecting 2.0 uL of benzene and toluene and 1.0 uL of BFB into 10 mL of methanol. The concentration of this stock is 175 ng/uL of benzene and toluene, and 150 ng/uL BFB. One microliter of the stock standard is injected onto a Tenax cartridge through a heated injection port set at 150°C. A GC oven can be used for this with the oven at room temperature. Helium carrier gas is set at 50 mL/min. The solvent flush technique should be used. After two min, remove the Tenax cartridge and place in the desorption heater for analysis. BFB is also used as an internal standard spike for GC/MS analysis which provides a good comparison between GC/FID and GC/MS. The results of this spike analysis should not vary more than 20 percent day to day. Initially and then periodically this spiked Tenax should be reanalyzed a second time to verify that the 10 min desorption time and 180-200°C temperature are adequate to remove all of the spiked components. It should be noted that only one spiked Tenax cartridge need be prepared and analyzed daily unless otherwise needed to ensure proper instrument operation.

An acceptable blank level is left to the discretion of the method analyst. An acceptable level is one that allows adequate determination of expected components emitted from the waste being burned.

4.4.3 After conditioning, traps are sealed and placed on cold packs until sampling is accomplished. Conditioned traps should be held for a minimum amount of time to prevent the possibility of contamination.

4.4.4 It may be useful to spike the Tenax and Tenax/charcoal traps with the compounds of interest to ensure that they can be thermally desorbed under laboratory conditions. After spiked traps are analyzed they may be reconditioned and packed for sampling.

4.5 Pretest preparation:

4.5.1 All train components shall be cleaned and assembled as previously described. A dry gas meter shall have been calibrated within 30 days prior to use, using an EPA-supplied standard orifice.

4.5.2 The VOST is assembled according to the schematic diagram in Figure 1. The cartridges should be positioned so that sample flow is

through the Tenax first and then the Tenax/charcoal. Cooling water should be circulated to the condensers and the temperature of the cooling water should be maintained near 0°C. The end caps of the sorbent cartridges should be placed in a clean screw-capped glass container during sample collection.

4.6 Leak-checking:

4.6.1 The train is leak-checked by closing the valve at the inlet to the first condenser and pulling a vacuum of 250 mm (10 in. Hg) above the normal operating pressure. The traps and condensers are isolated from the pump and the leak rate noted. The leak rate should be less than 2.5 mm Hg after 1 min. The train is then returned to atmospheric pressure by attaching a charcoal-filled tube to the train inlet and admitting ambient air filtered through the charcoal. This procedure will minimize contamination of the VOST components by excessive exposure to the fugitive emissions at hazardous waste incinerator sites.

4.7 Sample Collection

4.7.1 After leak-checking, sample collection is accomplished by opening the valve at the inlet to the first condenser, turning on the pump, and sampling at a rate of 1 liter/min for 20 min. The volume of sample for any pair of traps should not exceed 20 liters.

4.7.2 Following collection of 20 liters of sample, the train is leak-checked a second time at the highest pressure drop encountered during the run to minimize the chance of vacuum desorption of organics from the Tenax. The train is returned to atmospheric pressure, using the method discussed in Paragraph 4.1 and the two sorbent cartridges are removed. The end caps are replaced and the cartridges shall be placed in a suitable environment for storage and transport until analysis. The sample is considered invalid if the leak test does not meet specification.

4.7.3 A new pair of cartridges is placed in the VOST, the VOST leak-checked, and the sample collection process repeated as described above. Sample collection continues until six pairs of traps have been used.

4.7.4 All sample cartridges should be kept on cold packs until they are ready for analysis.

4.8 Blanks

4.8.1 **Field blanks/trip blanks:** Blank Tenax and Tenax/charcoal cartridges are taken to the sampling site and the end caps removed for the period of time required to exchange two pairs of traps on VOST. After the two VOST traps have been exchanged, the end caps are replaced on the blank Tenax and Tenax/charcoal tubes and these are returned to the cold packs and analyzed with the sample traps. At least one pair of field blanks (one Tenax, one Tenax/charcoal) shall be included with each

six pairs of sample cartridges collected (or for each field trial using VOST to collect volatile POHCs).

4.8.2 **Trip blanks:** At least one pair of blank cartridges (one Tenax, one Tenax/charcoal) shall be included with shipment of cartridges to a hazardous waste incinerator site. These "field blanks" will be treated like any other cartridges except that the end caps will not be removed during storage at the site. This pair of traps will be analyzed to monitor potential contamination which may occur during storage and shipment.

4.8.3 **Laboratory blanks:** One pair of blank cartridges (one Tenax, one Tenax/charcoal) will remain in the laboratory using the method of storage which is used for field samples. If the field and trip blanks contain high concentrations of contaminants (e.g., greater than 2 ng of a particular POHC), the laboratory blank shall be analyzed in order to identify the source of contamination.

5.0 CALCULATIONS (for sample volume)

5.1 The following nomenclature are used in the calculation of sample volume:

P_{bar} = Barometric pressure at the exit orifice of the dry gas meter, mm (in.) Hg.

P_{std} = Standard absolute pressure, 760 mm (29.92 in.) Hg.

T_m = Dry gas meter average absolute temperature, K (°R).

T_{std} = Standard absolute temperature, 293K (528°R).

V_m = Dry gas volume measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf).

γ = Dry gas meter calibration factor.

5.2 The volume of gas sampled is calculated as follows:

$$V_{m(std)} = V_m \gamma \frac{T_{std}\, P_{bar}}{T_m\, P_{std}} = K_1 \gamma \frac{V_m\, P_{bar}}{T_m}$$

where:

K_1 = 0.3858 K/mm Hg for metric units, or

K_1 = 17.64 °R/in. Hg for English units.

6.0 ANALYTICAL PROCEDURE

See Method 5040.

7.0 PRECISION AND ACCURACY REQUIREMENTS

7.1 Method Performance Check

Prior to field operation of the VOST at a hazardous waste incinerator, a method performance check should be conducted using either selected volatile POHCs of interest or two or more of the volatile POHCs for which data are available. This check may be conducted on the entire system (VOST/GC/MS) by analysis of a gas cylinder containing POHCs of interest or on only the analytical system by spiking of the POHCs onto the traps. The results of this check for replicate pairs of traps should demonstrate that recovery of the analytes fall within 50% to 150% of the expected values.

7.2 Performance Audit

During a trial burn a performance audit must be completed. The audit results should agree within 50% to 150% of the expected value for each specific target compound. This audit consists of collecting a gas sample containing one or more POHCs in the VOST from an EPA ppb gas cylinder. Collection of the audit sample in the VOST may be conducted either in the laboratory or at the trial burn site. Anaysis of the VOST audit sample must be by the same person, at the same time, and with the same analytical procedure as used for the regular VOST trail burn samples. EPA ppb gas cylinders currently available for VOST Audit are shown in Table 1 below.

The audit procedure, audit equipment and audit cylinder may be obtained by writing:

Audit Cylinder Gas Coordinator (MD-77B)
Quality Assurance Division
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

or by calling the Audit Cylinder Gas Coordinator at (919) 541-4531.

The request for the audit must be made at least 30 days prior to the scheduled trial burn. If a POHC is selected for which EPA does not have an audit cylinder, this audit is not required.

8.0 REFERENCES

1. Protocol for the Collection and Analysis of Volatile POHCs Using VOST. EPA/600/8-84/007, March 1984.

2. Sykes, A.L., Standard Operating Procedure for Blanking Tenax and Tenax/Charcoal Sampling Cartridges for Volatile Organic Sampling Train (VOST), Radion Corporation, P.O. Box 13000, Research Triangle Park, NC 27709.

3. Validation of the Volatile Organic Sampling Train (VOST) Protocol, Vols. I and II, EPA/600/4-86/014a, January 1986.

TABLE 1: Organic Gases in the ppb Audit Repository

Group I	Ranges of cylinders currently available:
5 Organics in N_2:	7 - 90 ppb
Carbon tetrachloride	90 - 430 ppb
Chloroform	430 - 10,000 ppb
Perchloroethylene	
Vinyl chloride	
Benzene	

Group II	Ranges of cylinders currently available:
9 Organics in N_2	7 - 90 ppb
Trichloroethylene	90 - 430 ppb
1,2-Dichloroethane	
1,2-Dibromoethane	
F-12	
F-11	
Bromomethane	
Methyl ethyl ketone	
1,1,1-Trichloroethane	
Acetronitrile	

TABLE 1: Organic Gases in the ppb Audit Repository (Continued)

Group III	Ranges of cylinders currently available:
7 Organics in N_2:	7 - 90 ppb
Vinylidene chloride	90 - 430 ppb
F-113	
F-114	
Acetone	
1,4-Dioxane	
Toluene	
Chlorobenzene	

Group IV	Ranges of cylinders currently available:
6 Organics in N_2:	7 - 90 ppb
Acrylonitrile	430 - 10,000
1,3-Butadiene	
Ethylene oxide	
Methylene chloride	
Propylene oxide	
Ortho-xylene	

CHAPTER ELEVEN

GROUND WATER MONITORING

11.1 BACKGROUND AND OBJECTIVES

The hazardous waste management facility permit regulations were promulgated in July, 1982 (40 CFR 265). Subpart F of these regulations, Ground Water Protection, sets forth performance standards for ground water monitoring systems at permitted facilities. Performance standards were selected, rather than design and operating standards, because of the diversity of designs and practices appropriate in various site-specific situations. Performance standards provide more flexibility than design and operating standards because site-specific conditions can be accomodated case by case without variance procedures. However, implementation is less efficient because permit writers may need to consider a wider variety of designs and practices; furthermore, much of the variation in reported values is attributable to the variety of designs and practices currently in use.

The purpose of this Chapter is to identify certain designs and practices which meet the performance requirements in specified situations. One of the Agency's reasons for doing so is to encourage the use of more standard methods. The designs and practices which are identified as acceptable in this chapter are considered to be acceptable for the uses and conditions specified. Therefore, permit applicants need not justify their selection. Use of these designs and practices is not mandatory; owners and operators may submit applications based on other approaches. The only incentive to use the "acceptable" designs and practices is that they are already recognized by the Agency and so they need not be justified again. As this list matures, the Agency is hopeful that sources of variance due to the variety in methodology will decrease.

The provisions of this Chapter were developed recognizing that professional judgement will always be needed in designing effective monitoring systems. But, for efficiency of operation, repeated patterns of acceptance and rejection of designs and operations are identified so that the lengthy documentation need not be repeated each time. Readers will note that there are many arbitrary criteria for some "acceptable" methods and that there is little or no attempt to justify the cut-off values. This is intended. This Chapter is expected to be a living document, cautiously developed. As new criteria become identified further refinements of these values should be expected. The purposes of listing the acceptable designs and practices are to encourage use of standard techniques by making their use easier and to reduce the burden on the applicants by relieving their need to justify use of proven designs or practices. The listing establishes, in essence, blanket approvals for a limited number of techniques in those conditions for which they are known to be acceptable.

This Subsection establishes certain ground water sampling system designs and practices as being acceptable under certain conditions for use in meeting

the requirements of Subpart F (264.90 et seq.). It also lists certain practices and designs which are not acceptable. The acceptable designs and practices are listed in Paragraph 11.4, below, with specified conditions for which each may be acceptable. The proscribed practices and designs are listed in Paragraph 11.5. These are not acceptable for use in satisfaction of the permit requirements; petitions for their use must follow normal channels.

11.2 RELATIONSHIP TO THE REGULATIONS AND TO OTHER DOCUMENTS.

The regulations in Subpart F will continue to be the sole location of the performance standards for ground water monitoring systems. The provisions of this Chapter only establish the acceptability of a limited number of designs or operations. The Chapter is not intended to replace the regulations or the guidance documents which explain application of the regulations in the particular, or site-specific, situation. It is related to the guidance documents in that it will promote use of the more established procedures found in general guidance.

The contents of this Chapter will be taken from general enforcement and permitting guidance documents, and it is intended that these be consistent with all RCRA ground water monitoring guidance. The specific conditions given for the acceptable designs and precedures may not be found in the several guidance documents from which those designs and procedures are taken. Many of these conditions are arbitrarily selected. They are based on the experience of permit writers and enforcement officials. Since the conditions only affect procedural issues (whether the selection is justified or not) the rigor of their development has not been as extensive as if they were requirements.

There is one preeminent RCRA guidance document for ground water monitoring at this time: The Technical Enforcement Guidance Document. (The TEGD, finalized September 1986, is available from the Office of Waste Programs Enforcement, (202)-475-9328). This document is written for enforcement officials' use in implementing the interim status provisions, 265.90 et seq., but most of the hydrogeologic principles apply directly to permitted facilities as well as to those in interim status. The TEGD is the major source of concepts for this chapter; it is and will be the major repository of RCRA ground water monitoring principles. It is intended that nothing in this chapter conflicts with the TEGD.

Other ground water monitoring guidance documents are in circulation. Several, such as "Ground Water Monitoring Guidance for Owners and Operators of Interim Status Facilities," have been superceded by the TEGD. Others, such as the draft "Permit Writers Guidance for Ground Water Monitoring," have never been finalized and do not fully reflect Agency policy.

Other documents which may be of interest are as follows:

1. Barcelona, Michael J., James P. Gibb and Robin A. Miller, A Guide to the Selection of Materials for Monitoring Well Construction and Ground Water Sampling, Illinois State Water Survey Contract Report (ISWS) #327, EPA Contract No. EPA CR-809966-01, August 1983.

2. Benson, R.C., R.A. Glaccum, and M. R. Noel, Geophysical Techniques for Sensing Buried Waste and Waste Migration, Technos, Inc., EPA Contract No. 68-03-3050; available from National Water Well Association, Worthington, OH.

3. Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EMSL, Cincinnati, EPA-600-4-79-019, March 1979 and subsequent revisions; available from EMSL, Cincinnati, OH.

4. Hazardous Waste Ground Water Task Force, Protocol for Ground Water Inspections at Hazardous Waste Treatment Storage and Disposal Facilities, April 1986.

5. Methods for the Storage and Retrieval of RCRA Ground Water Monitoring Data on STORET, Ref. Storet User Support (800-488-5985).

6. Methods of Chemical Analysis of Water and Wastes, EMSL, Cincinnati, EPA-600/4-79-020, Revised March 1983; available from EMSL, Cincinnati, OH.

7. Plumb, R.H., and C.K. Fitzsimmons, Performance Evaluation of RCRA Indicator Parameters for Ground Water Monitoring, Proceedings of the First Canadian-American Conference on Hydrogeology, National Water Well Association, Worthington, OH, pp. 129-137, June 1984.

8. A Practical Guide for Ground Water Sampling, ERL, ADA, OK, EPA/600/2-85/104, Sept. 1, 1985; available from Illinois State Water Survey, Champagne, IL.

11.3 REVISIONS AND ADDITIONS

This Chapter will be revised from time to time as new technological developments and experience dictate. Each revision will be proposed before being finalized, and there will be ample time before the effective date for the revisions to be incorporated into future designs.

Applicants desiring to add particular designs or practices to the "acceptable" list, either for their own unique situation or as general provisions, or to use designs or practices on the "proscribed" list may do so by petitions.

11.4 ACCEPTABLE DESIGNS AND PRACTICES

The following designs and practices are acceptable, in the conditions described and for the purposes listed, without need for justification. Permit writers may question the existence of the condition or the definition of purpose, but not the use of the design or practice once conditions and purposes are established.

11.4.1 Site Characterisation

(a) Borehole location patterns, designed by qualified geologists, are acceptable for site characterization. Such characterizations are for general delineation of stratigraphy and flow paths and for establishing initial design of well placement, screen length, depth, etc.
Conditions: When unexpected discontinuities of major strata or pathways do not occur.

(b) Geophysical logging and other indirect measurement techniques may be used in site characterization for the limited purpose of augmenting direct observation of cuttings and corings by professional geologists.
Conditions: None.

(c) Quarterly measurements are generally satisfactory for establishing seasonal and temporal variations in flow velocity and direction for purposes of assuring that the elevations of screens are correct, of documenting the appropriateness of background well locations, and of assuring coverage of all possible downgradient pathways.
Conditions: None.

11.4.2 Well Location, Design, and Construction

(a) Downgradient well locations which result in placement in potential pathways of contaminant migration are acceptable for routine detection sampling programs. The density will vary based on the size of the pathway.
Conditions: When site characterization confirms simple homogenous hydrogeology, without discontinuities or faults in the vicinity of the wells, and when folds and fractures are not expected to channel flows past well intakes.

(b) Monitoring well screen lengths should generally not cut across several flow zones but rather furnish depth-discrete measurements. These conditions are acceptable for the purpose of obtaining samples which represent ground water quality at the point of compliance.
Conditions: When the strata of concern is $\geq$ 10' thick.

(c) Use of air rotary drilling methods is acceptable for installing monitoring wells.
Conditions: Except when drilling through contaminated upper horizons, unless precautions are taken.

(d) Fluorocarbon resins (PTFE, PFA, FEP, etc.) and stainless steel (304 or 316) are acceptable materials for sample-contact surfaces in new or replacement monitoring wells where potentially sorbing organics are of concern.
Conditions: Stainless steel may only be used in non-corrosive conditions. All new or replacement wells to be installed at a given time should be of the same material.

(e) Existing wells which do not meet the recommendations in guidance for materials or installation may be proposed for inclusion in the permit.

Conditions: When documented to be free of bias by pairing new PTFE OR stainless wells with, for instance, at least ten percent of the old, existing wells.

11.4.3 Sampling

(a) The field quality control procedures contained in Reference 4, Section 11.2 above, and those specified in Chapters 1 and 9 of this document are the only acceptable procedures.

(b) Well evacuation measured at three times the computed well casing volume is acceptable for assuring that the sample contains ground water representative of the formation.

Conditions: Evacuation measured to ±5% of the computed volume based on water surface elevation and well bottom measured immediately prior to evacuation.

(c) Samples containing less than 5 N.T.U. turbidity are acceptable for analysis when the analytic method is sensitive to turbidity (such as the analysis of metals). Samples containing greater than 5 N.T.U. are only acceptable when well development is certified by a qualified hydrogeologist as the best obtainable.

Conditions: Turbidity evaluation must accompany all potentially affected values.

(d) The sample preservation techniques presented in Table 11-1 are acceptable.

(e) The scheduled time interval between sample collections should not be greater than the computed time of travel either from the upgradient wells to the point of compliance or from the point of compliance to the property boundary.

(f) Evacuation of the well to dryness is an acceptable procedure to ensure that the sample contains representative ground water.

Conditions: When the recharge is so slow that the well will yield fewer than three well volumes before dryness but fast enough that the recharging water will not cascade down the inside of the casing.

11.4.4 Analysis and Reporting

The codes listed in Table 11-2 may be used for purposes and conditions listed.

11.5 UNACCEPTABLE DESIGNS AND PRACTICES

The following designs and practices are unacceptable in the conditions or for the purposes specified.

11.5.1 Site Characterization

Use of unsubstantiated data not meeting quality assurance criteria may not be used other than in support of general trends or to establish relationships between parameters.

Conditions: All conclusions and findings based on unconfirmed data and unsupported by quality controlled data are inadmissable as support for permit conditions or stipulations.

11.5.2 Well Location, Design, and Construction

Fabric filters should not be used as filter pack material.

11.5.3 Sampling

(a) The following devices are not generally acceptable for collecting samples for analysis:

1. Gas driven piston pump.
2. Suction lift pumps.
3. Submersible diaphragm.
4. Gas lift samplers.
5. Impeller pumps.

(b) Data obtained by unsubstantiated techniques and procedures not meeting quality assurance criteria or not conforming to quality control procedures may not be used except when attempting to describe pre-existing site conditions which are no longer observable.

11.5.4 Data Evaluation and Comparisons

Pooling upgradient or background values from diverse hydrogeologic strata in a manner which combines data from discrete or distinct sampling locations as though they were points along a continuous spectrum is not acceptable. All up-down comparisions must be between samples taken from common flow paths.

TABLE 11-1

SAMPLING AND PRESERVATION PROCEDURES FOR DETECTION MONITORING[a]

Parameter	Recommended Container[b]	Preservative	Maximum Holding Time	Minimum Volume Required for Analysis
		Indicators of Ground Water Contamination[c]		
pH	T, P, G	Field determined	None	25 mL
Specific conductance	T, P, G	Field determined	None	100 mL
TOC	G, Teflon-lined cap	Cool 4°C, HCl to pH <2	28 days	4 x 15 mL
TOX	G, amber, Teflon-lined cap	Cool 4°C, add 1 mL of 1.1M sodium sulfite	7 days	4 x 15 mL
		Ground Water Quality Characteristics		
Chloride	T, P, G	4°C	28 days	50 mL
Iron Manganese Sodium	T, P	Field acidified to pH <2 with HNO_3	6 months	200 mL
Phenols	G	4°C/H_2SO_4 to pH <2	28 days	500 mL
Sulfate	T, P, G	Cool, 4°C	28 days	50 mL
		EPA Interim Drinking Water characteristics		
Arsenic Barium Cadmium Chromium Lead Mercury Selenium Silver	T, P Dark Bottle	Total Metals Field acidified to pH <2 with HNO_3 Dissolved Metals 1. Field filtration (0.45 micron) 2. Acidify to pH <2 with HNO_3	6 months 6 months	1,000 mL 1,000 mL
Fluoride	T, P	Field acidified to pH <2 with HNO_3	28 days	300 mL
Nitrate	T, P, G	4°C/H_2SO_4 to pH <2	14 days	1,000 mL

(Continued)

TABLE 11-1 (Continued)

SAMPLING AND PRESERVATION PROCEDURES FOR DETECTION MONITORING[a]

Parameter	Recommended Container[b]	Preservative	Maximum Holding Time	Minimum Volume Required for Analysis
Endrin Lindane Methoxychlor Toxaphene 2,4 D 2,4,5 TP Silvex	T, G	Cool, 4°C	7 days	2,000 mL
Radium Gross Alpha Gross Beta	P, G	Field acidified to pH <2 with HNO_3	6 months	1 gallon
Coliform bacteria	PP, G (sterilized)	Cool, 4°C	6 hours	200 mL
	Other Ground Water Characteristics of Interest			
Cyanide	P, G	Cool, 4°C, NaOH to pH >12	14 days	500 mL
Oil and Grease	G only	Cool, 4°C H_2SO_4 to pH <2	28 days	100 mL
Semivolatile, volatile organics	T, G	Cool, 4°C	7 days	1,000 mL

[a]References: Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, SW-846 (3rd edition, 1986).
Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020.
Standard Methods for the Examination of Water and Wastewater, 16th edition (1985).

[b]Container Types:
P = Plastic (polyethylene)
G = Glass
T = Teflon
PP = Polypropylene

[c]Based on the requirements for detection monitoring (265.93), the owner/operator must collect a sufficient volume of ground water to allow for the analysis of four separate replicates.

TABLE 11-2
A LISTING AND DESCRIPTION OF CODES USED TO INDICATE THAT POLLUTANT CONCENTRATIONS WERE BELOW A CONCENTRATION WHICH CAN BE MEASURED ACCURATELY OR THAT THE POLLUTANTS WERE NOT PRESENT

Codes	Definition of the Acronyms	Examples of Use	Used to Indicate That the Pollutant Was Less Than a Limit of Detection	Used to Indicate That the Pollutant Was not Present
LOD+	Limit of detection	LOD 0.421	Yes	No
LOQ+	Limit of quantification	LOQ 2.234	Yes	No
MDL++	Method detection limit	MDL 0.631	Yes	No
LT	Less than	LT, LT 0.01 LT 0.148	Yes	No
BDL	Below detection limit	BDL, BDL 0.01 BDL 0.148	Yes	No
<		<0.01, <0.148	Yes	No
Negative signs		-0.01, -0.148	Yes	No
Trace*		Trace, T	Yes	No
K		K0.01, K0.148	Yes	No
ND*	Not detected	ND	Yes	Yes
Dashes*		—	Yes	Yes
Large numbers*		999999	Yes	Yes
Zeros*		0	Yes	Yes
Blanks*			Yes	Yes

NOTES:
1. The codes marked with a + are the codes used when the American Chemical Society methodology is applied.
2. The code marked with a ++ is the code that is used when the 40 CFR 136 methodology is applied.
3. The Codes column lists examples of low concentration designations that may be included in data submissions.
4. Several codes, marked with a *, have potential for being ambiguous. Their meaning depends on laboratory reporting protocols and could either indicate that the value was LT a limit of detection or not present.

CHAPTER TWELVE

LAND TREATMENT MONITORING

12.1 BACKGROUND

A monitoring program is an essential component at any land treatment unit and should be planned to provide assurance of appropriate facility design, to act as a feedback loop to furnish guidance on improving unit management, and to indicate the rate at which the treatment capacity is being approached. Because many assumptions must be made in the design of a land treatment unit, monitoring can be used to verify whether the initial data and assumptions were correct or if design or operational changes are needed. Monitoring cannot be substituted for careful design based on the fullest reasonable understanding of the effects of applying hazardous waste to the soil; however, for existing Hazardous Waste Land Treatment (HWLT) units (which must retrofit to comply with regulations), monitoring can provide much of the data base needed for demonstrating treatment.

Figure 12-1 shows the topics to be considered when developing a monitoring program. The program must be developed to provide the following assurances:

1. that the waste being applied does not deviate significantly from the waste for which the unit was designed;

2. that waste constituents are not leaching from the land treatment area in unacceptable concentrations;

3. that ground water is not being adversely affected by the migration of hazardous constituents of the waste(s); and

4. that waste constituents will not create a food-chain hazard if crops are harvested.

12.2 TREATMENT ZONE

As is depicted in Figure 12-2, the entire land treatment operation and monitoring program revolve about a central component, the treatment zone. Concentrating on the treatment zone is a useful approach to describing and monitoring a land treatment system. The treatment zone is the soil to which wastes are applied or incorporated; HWLT units are designed so that degradation, transformation, and immobilization of hazardous constituents and their metabolites occur within this zone.

In practice, setting a boundary to the treatment zone is difficult. In choosing the boundaries of the treatment zone, soil-forming processes and the associated decrease in biological activity with depth should be considered.

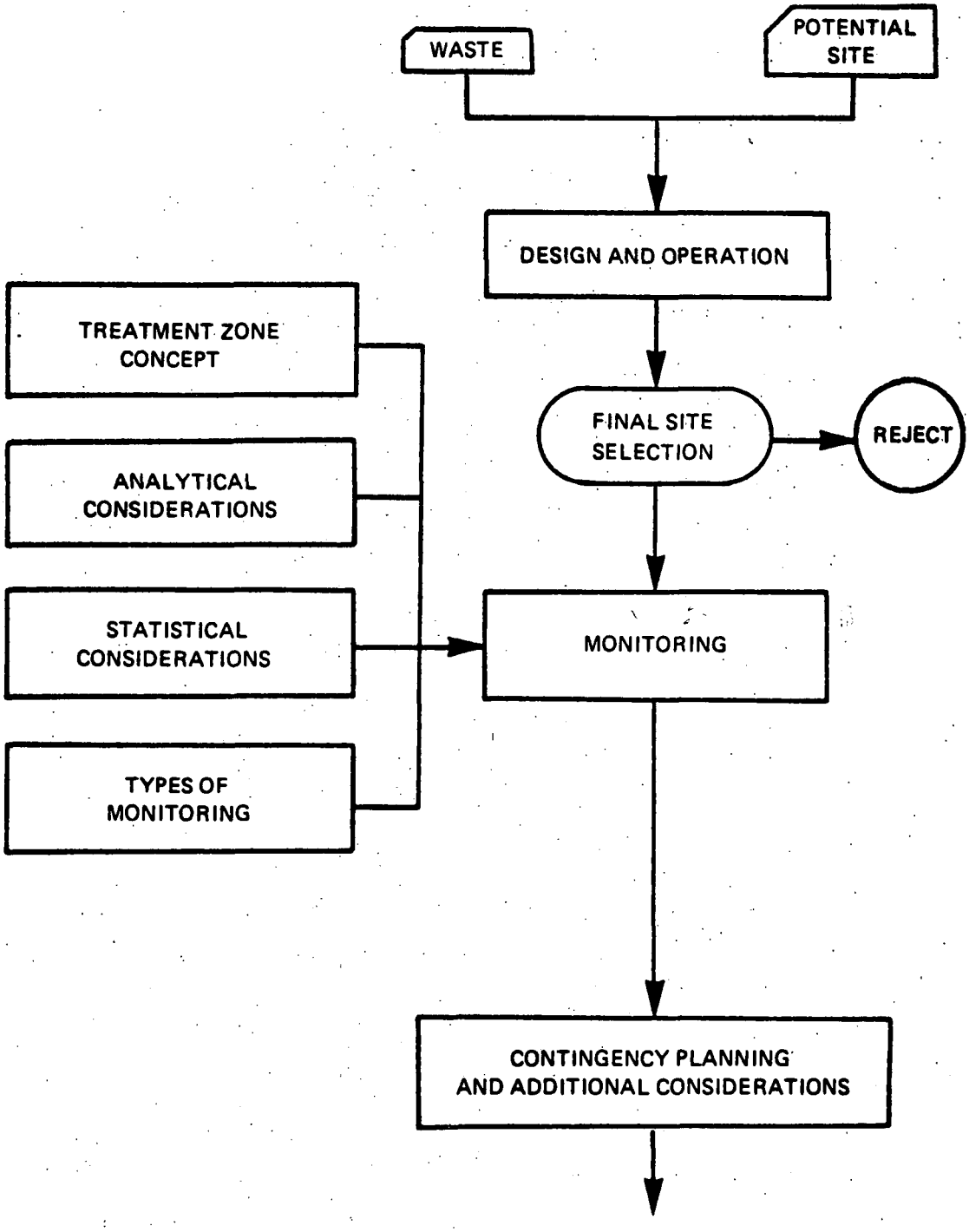


Figure 12-1. Topics to be considered in developing a monitoring program for an HWLT unit.

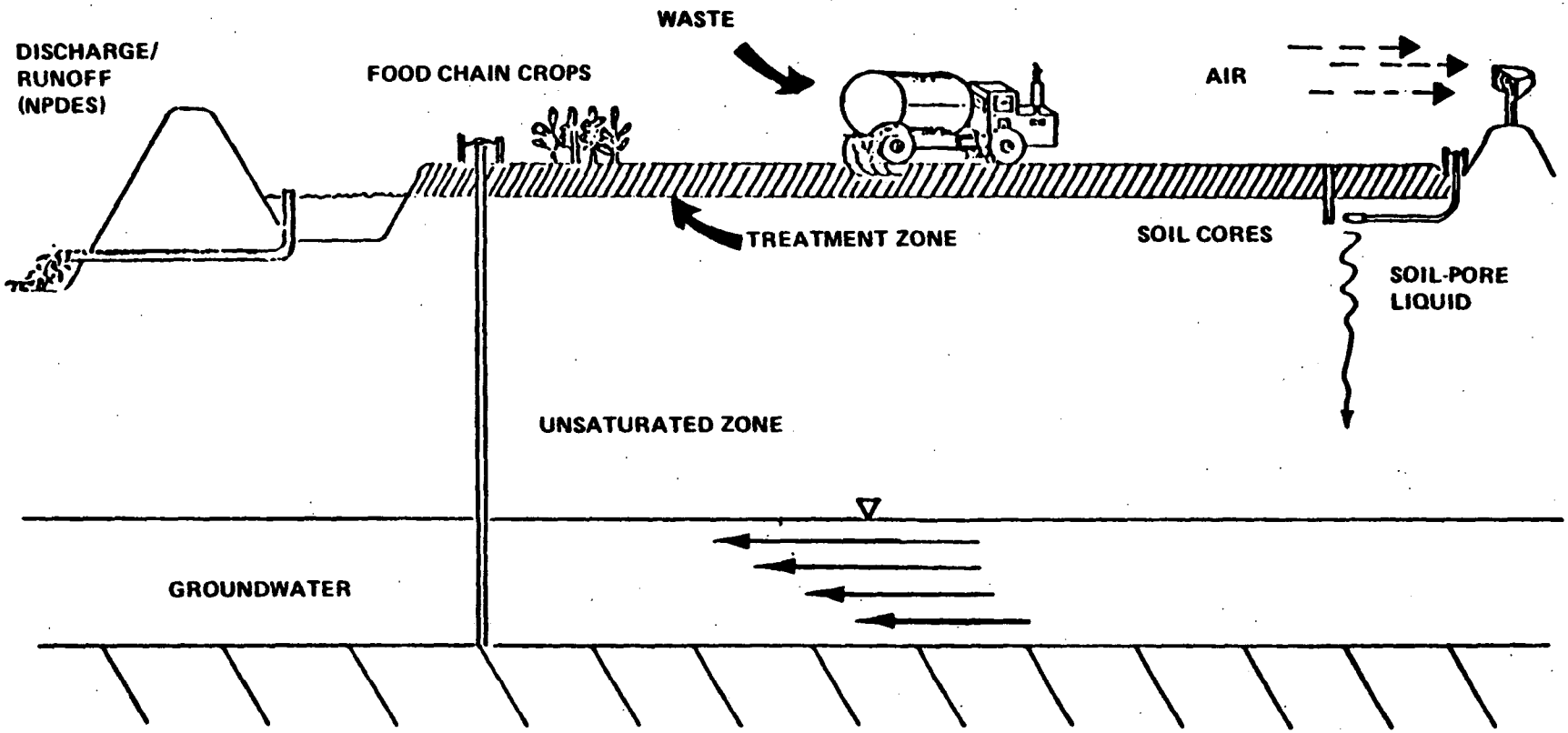


Figure 12-2. Various types of monitoring for land treatment units.

12.3 REGULATORY DEFINITION

The current regulations (U.S. EPA, 1982a) require the following types of monitoring:

1. Ground water detection monitoring to determine if a leachate plume has reached the edge of the waste management area (40 CFR 264.98).

2. Ground water compliance monitoring to determine if the facility is complying with ground water protection standards for hazardous constituents (40 CFR 264.99).

3. Monitoring of soil pH and concentration of cadmium in the waste when certain food-chain crops are grown on HWLT units where cadmium is disposed of (40 CFR 264.276).

4. Unsaturated zone monitoring, including soil cores and soil-pore liquid monitoring, to determine if hazardous constituents are migrating out of the treatment zone (40 CFR 246.278).

5. Waste analysis of all types of waste to be disposed at the HWLT unit (40 CFR 264.13).

12.4 MONITORING AND SAMPLING STRATEGY

As discussed earlier, the monitoring program centers around the treatment zone.

The frequency of sampling and the parameters to be analyzed depend on the characteristics of the waste being disposed, the physical layout of the unit, and the surface and subsurface characteristics of the site. Table 12-1 provides guidance for developing an operational monitoring program. Each of the types of monitoring is discussed below.

12.4.1 Waste Monitoring and Sampling Strategy

Waste streams need to be routinely sampled and tested to check for changes in composition. A detailed description of appropriate waste sampling techniques, tools, procedures, etc., is provided in Chapter Nine of this manual (in Part III, Sampling). These procedures should be followed during all waste sampling events. Waste analysis methods are provided in this manual. The analyst should choose the appropriate method, based on each waste and specific constituents to be tested for.

The frequency with which a waste needs to be sampled and the parameters to be analyzed depend greatly on the variables that influence the quantity and quality of the waste. When waste is generated in a batch, as would be expected from an annual or biannual cleanout of a lagoon or tank, the waste should be fully characterized prior to each application. When the waste is

TABLE 12-1 GUIDANCE FOR AN OPERATIONAL MONITORING PROGRAM AT HWLT UNITS

Media to be Monitored	Purpose	Sampling Frequency	Number of Samples	Parameters to be Analyzed
Waste	Quality Change.	Quarterly composites if continuous stream; each batch if intermittent generation.	One	At least rate and capacity limiting constituents, plus those within 25% of being limiting, principal hazardous constituents, pH and EC.
Soil cores (unsaturated zone)	Determine slow movement of hazardous constituents.	Quarterly	One composited from two per 1.5 ha (4 ac); minimum of 3 composited from 6 per uniform area.	All hazardous constituents in the waste or the principal hazardous constituents, metabolites of hazardous constituents, and nonhazardous constituents of concern.
Soil-pore liquid (unsaturated zone)	Determine highly mobile constituents.	Quarterly, preferably following leachate generating precipitation snowmelt.	One composited from two samplers per 1.5 ha (4 ac); minimum of 3 composited from 6 per uniform area.	All hazardous constituents in the waste or the principal hazardous constituents, mobile metabolites of hazardous constituents, and important mobile nonhazardous constituents.
Groundwater	Determine mobile constituents.	Semiannually	Minimum of four suggested--one upgradient, three downgradient.	Hazardous constituents and metabolites or select indicators.
Vegetation (if grown for food chain use).	Phytotoxic and hazardous transmitted constituents (food chain hazards).	Annually or at harvests.	One per 1.5 ha (4 ac) or three of processed crop before sales.	Hazardous metals and organics and their metabolites.
Runoff water	Soluble or suspended constituents.	As required for NPDES permit.	As permit requires, or one.	Discharge permit and background parameters plus hazardous organics.
Soil in the treatment zone	Determine degradation, pH, nutrients, and rate and capacity limiting constituents.	Quarterly	7-10 composited to one per 1.5 ha (4 ac).	
Air	Personnel and population health hazards.	Quarterly	Five	Particulates (adsorbed hazardous constituents) and hazardous volatiles.

generated more nearly continuously, samples should be collected and composited based on a statistical design over a period of time to ensure that the waste is of a uniform quality. For example, wastes that are generated continuously could be sampled weekly or daily on a flow-proportional basis and composited and analyzed quarterly or monthly. When no changes have been made in the operation of the plant or the treatment of the waste which could significantly alter concentration of waste constituents, the waste should, at a minimum, be analyzed for (1) the constituents that restrict the annual application rates (RLC) and the allowable cumulative applications (CLC), (2) the constituents that are within 25% of the level at which they would be limiting, and (3) all other hazardous constituents that have been shown to be present in the waste in the initial waste characterization. Because synergism and antagonism as well as unlisted waste metabolites can create hazards that cannot be described by chemical analysis alone, routine multigenicity testing may be performed if the treatment demonstration has indicated a possible problem. In addition, waste should be analyzed as soon as possible after a change in operations that could affect the waste characteristics.

12.4.2 Ground Water Monitoring and Sampling Strategy

To ensure that irreparable ground water damage does not occur as a result of HWLT, it is necessary that the ground water quality be monitored. Ground water monitoring supplements the unsaturated zone monitoring system but does not replace it. A contamination problem first detected in the leachate water may indicate the need to alter the management program, and ground water can then be observed for the same problem. It is through the successful combination of these two systems that accurate monitoring of vertically moving constituents can be achieved. Ground water monitoring requirements are discussed in Chapter Eleven of this manual.

12.4.3 Vegetation Monitoring and Sampling Strategy

Where food-chain crops are to be grown, analysis of the vegetation at the HWLT unit will aid in ensuring that harmful quantities of metals or other waste constituents are not being accumulated by, or adhering to surfaces of, the plants. Although a safety demonstration before planting is required (U.S. EPA, 1982a), operational monitoring is recommended to verify that crop contamination has not occurred. Vegetation monitoring is an important measurement during the post-closure period where the area may possibly be used for food or forage production. Sampling should be done annually or at each harvest. The concentrations of metals and other constituents in the vegetation will change with moisture content, stage of growth, and the part of the plant sampled, and thus results must be carefully interpreted. The number of samples to analyze is again based on a sliding scale similar to that used for sampling soils. Forage samples should include all aerial plant parts, and the edible parts of grain, fruit, or vegetation crops should be sampled separately.

12.4.4 Runoff Water Monitoring and Sampling Strategy

If runoff water analyses are needed to satisfy NPDES permit conditions (National Pollution Discharge Elimination System, U.S. EPA, 1981), a monitoring program should be instituted. This program would not be covered under RCRA hazardous waste land disposal requirements, but it would be an integral part of facility design. The sampling and monitoring approach will vary, depending on whether the water is released as a continuous discharge or as a batch discharge following treatment to reduce the hazardous nature of the water. Constituents to be analyzed should be specified in the NPDES permit.

When a relatively continuous flow is anticipated, sampling must be flow proportional. A means of flow measurement and an automated sampling device are a reasonable combination for this type of monitoring. Flow can be measured using a weir or flume (U.S.D.A., 1979) for overload flow-water pretreatment systems and packaged water treatment plants, and in-line flow measurement may be an additional option on the packaged treatment systems. The sampling device should be set up to obtain periodic grab samples as the water passes through the flow-rate measuring device. A number of programmable, automated samplers that can take discrete or composite samples are on the market.

For batch treatment, such as mere gravity separation or mechanically aerated systems, flow is not so important as is the hazardous constituent content of each batch. Sampling before discharge would, in this case, involve manual pond sampling, using multiple grab samples. The samples would preferably represent the entire water column to be discharged in each batch rather than a single depth increment. Statistical procedures should again be used for either treatment and discharge approach.

12.4.5 Unsaturated Zone Monitoring and Sampling Strategy

The unsaturated zone is described as the layer of soil or parent material separating the bottom of the treatment zone and the seasonal high-water table or ground water table and is usually found to have a moisture content less than saturation. In this zone, the movement of moisture may often be relatively slow in response to soil properties and prevailing climatic conditions; however, in some locations, soils and waste management practices may lead to periods of heavy hydraulic loading that could cause rapid downward flux of moisture.

An unsaturated zone monitoring plan should be developed for two purposes: (1) to detect any significant movement of hazardous constituents out of the system, and (2) to furnish information for management decisions. In light of the variability in soil-water flux and the mobility of hazardous waste constituents, the unsaturated zone monitoring plan should include sampling the soil to evaluate relatively slow-moving waste constituents (soil core monitoring) and sampling the soil-pore liquid to evaluate fast-moving waste constituents. Monitoring for hazardous constituents should be performed on a representative background plot(s) until background levels are established and

immediately below the treatment zone (active portion). The number, location, and depth of soil core and soil-pore liquid samples taken must allow an accurate indication of the quality of soil-pore liquid and soil below the treatment zone and in the background area. The frequency and timing of soil-pore liquid sampling must be based on the frequency, time, and rate of waste application; proximity of the treatment zone to ground water; soil permeability; and amount of precipitation. The data from this program must be sufficient to determine if statistically significant increases in hazardous constituents (or selected indicator constituents) have occurred below the treatment zone. Location and depth of soil core and soil-pore liquid samples follow the same reasoning, but the number, frequency, and timing of soil core sampling differs somewhat from that required for soil-pore liquid sampling. Thus, the unique aspects of these topics will be considered together with discussions of techniques for obtaining the two types of samples.

12.4.5.1 Location of Samples

Soil characteristics, waste type, and waste application rate are all important factors in determining the environmental impact of a particular land treatment unit or part of a unit on the environment. Therefore, areas of the land treatment unit for which these characteristics are similar (i.e., uniform areas) should be sampled as a single monitoring unit. A uniform area is defined as an area of the active portion of a land treatment unit which is composed of soils of the same soil series (U.S.D.A., 1975) and to which similar wastes or waste mixtures are applied at similar application rates. If, however, the texture of the surface soil differs significantly among soils of the same series classification, the phase classification of the soil should be considered in defining "uniform areas." A certified professional soil scientist should be consulted in designating uniform areas.

Based on that definition, it is recommended that the location of soil core sampling or soil-pore liquid monitoring devices within a given uniform area be randomly selected. Random selection of samples ensures a more accurate representation of conditions within a given uniform area. It is convenient to spot the field location for soil core and soil-pore liquid devices by selecting random distances on a coordinate system and using the intersection of the two random distances as the location at which a soil core should be taken or a soil-pore liquid monitoring device installed. This system works well for fields of both regular and irregular shape because the points outside the area of interest are merely discarded and only the points inside the area are used in the sample.

The location within a given uniform area of a land treatment unit (i.e., active portion monitoring) at which a soil core should be taken or a soil-pore liquid monitoring device installed should be determined using the following procedure:

1. Divide the land treatment unit into uniform areas under the direction of a certified professional soil scientist.

2. Set up coordinates for each uniform area by establishing two base lines at right angles to each other which intersect at an arbitrarily selected origin, for example, the southwest corner. Each baseline should extend far enough for all of the uniform area to fall within the quadrant.

3. Establish a scale interval along each base line. The units of this scale may be feet, yards, meters, or other units, depending on the size of the uniform area, but both base lines should have the same units.

4. Draw two random numbers from a random-number table (available in most basic statistics books). Use these numbers to locate one point along each of the base lines.

5. Locate the intersection of two lines drawn perpendicular to the base lines through these points. This intersection represents one randomly selected location for collection of one soil core, or for installation of one soil-pore liquid device. If this location at the intersection is outside the uniform area, disregard and repeat the above procedure.

6. For soil core monitoring, repeat the above procedure as many times as necessary to obtain the desired number of locations within each uniform area of the land treatment unit. This procedure for randomly selecting locations must be repeated for each soil core sampling event but will be needed only once in locating soil-pore liquid monitoring devices.

Locations for monitoring on background areas should also be randomly determined. Again, consult a certified professional soil scientist in determining an acceptable background area. The background area must have characteristics (including soil series classification) similar to those present in the uniform area of the land treatment unit it is representing, but it should be free from possible contamination from past or present activities that could have contributed to the concentrations of the hazardous constituents of concern. Establish coordinates for an arbitrarily selected portion of the background area and use the above procedure for randomly choosing sampling locations.

12.4.5.2 Depth of Samples

Because unsaturated zone monitoring is intended to detect pollutant migration from the treatment zone, samples should logically be obtained from immediately below this zone. Care should be taken to ensure that samples from active areas of the land treatment unit and background samples are monitoring similar horizons or layers of parent material. Because soils seldom consist of smooth, horizontal layers, but are often undulating, sloped, and sometimes discontinuous, it would be unwise to specify a single depth below the land surface to be used for comparative sampling. A convenient method for choosing

sampling depths is to define the bottom of the treatment zone as the bottom of a chosen diagnostic solid horizon and not as a rigid depth. Sampling depth would then be easily defined with respect to the bottom of the treatment zone. At a minimum, soil core and soil-pore liquid sampling should monitor within 30 cm (12 in.) of the bottom of the treatment zone. Additional sampling depths may be desirable, for instance, if analytical results are inconclusive or questionable. Core samples should include only the 0- to 15-cm increment below the treatment zone, whereas soil-pore liquid samplers should be placed so that they collect liquid from anywhere within this 30-cm zone.

12.4.5.3 Soil Core Sampling Techniques

Soil Cores

Waste constituents may move slowly through the soil profile for a number of reasons, such as the lack of sufficient soil moisture to leach through the system, a natural or artificially occurring layer or horizon of low hydraulic conductivity, or waste constituents that exhibit only a low to moderate mobility relative to water in soil. Any one or a combination of these effects can be observed by soil core monitoring. Based on the treatment zone concept, only the portions of soil cores collected below the treatment zone need to be analyzed. The intent is to demonstrate whether there are significantly higher concentrations of hazardous constituents in material below the treatment zone than in background soils or parent material.

Soil core sampling should proceed according to a definite plan with regard to number, frequency, and technique. Previous discussions of statistical considerations should provide guidance in choosing the number of samples required. Background values for soil core monitoring should be established by collecting at least eight randomly selected soil cores for each soil series present in the treatment zone. These samples can be composited in pairs (from immediately adjacent locations) to form four samples for analysis. For each soil series, a background arithmetic mean and variance should be calculated for each hazardous constituent. For monitoring the active portion of the land treatment facility, a minimum of six randomly selected soil cores should be obtained per uniform area and composited, as before, to yield three samples for analysis. If, however, a uniform area is >5 ha (12 ac), at least two randomly selected soil cores should be taken per 1.5 ha (4 ac) and composited in pairs based on location. Data from the samples in a given uniform area should be averaged and statistically compared. If analyses reveal a large variance from samples within a given uniform area, more samples may be necessary. Soil coring should be done at least semiannually, except for background sampling, which, after background values are established, may be performed as needed to determine if background levels are changing over time.

It is important to keep an accurate record of the locations from which soil core samples have been taken. Even when areas have been judged to be uniform, the best attempts at homogeneous waste application and management cannot achieve perfect uniformity. It is probable in many systems that small problem areas, or "hot spots," may occur, causing localized real or apparent pollutant migration. Examples of "apparent" migration might include small

areas where waste was applied too heavily or where the machinery on-site mixed waste too deeply. The sampling procedure itself is subject to error and so may indicate apparent pollutant migration. Therefore, anomalous data points can and should be resampled at the suspect location(s) to determine if a problem exists, even if the uniform area as a whole shows no statistically significant pollutant migration.

The methods used for soil sampling are variable and depend partially on the size and depth of the sample needed and the number and frequency of samples to be taken. Of the available equipment, oil field augers are useful if small samples need to be taken by hand, and bucket augers give larger samples. Powered coring or drilling equipment, if available, is the preferable choice because it can rapidly sample to the desired depths and provide a clean, minimally disturbed sample for analysis. Due to the time involved in coring to 1.5 m, and sometimes farther, powered equipment can often be less costly than hand sampling. In any case, extreme care must be taken to prevent cross contamination of samples. Loose soil or waste should be scraped away from the surface to prevent it from contaminating samples collected from lower layers. The material removed from the treatment zone portion of the borehole can be analyzed, if desired, to evaluate conditions in the treatment zone. It is advisable to record field observations of the treatment zone even if no analysis is done. Finally, boreholes absolutely must be backfilled carefully to prevent hazardous constituents from channeling down the hole. Native soil compacted to about field bulk density, clay slurry, or other suitable plug material may be used.

Sample handling, preservation, and shipment should follow a chain-of-custody procedure and a defined preservation method such as is found in Chapter Nine of this manual or in the analytical section of EPA document SW-874, Hazardous Waste Land Treatment (U.S. EPA, 1983). If more sample is collected than is needed for analysis, the volume should be reduced by either the quartering or riffle technique. (A riffle is a sample-splitting device designed for use with dried ground samples.)

The analysis of soil cores must include all hazardous constituents that are reasonably expected to leach or the principal hazardous constituents (PHCs) that generally indicate hazardous constituent movement (U.S. EPA, 1982a).

Soil-Pore Liquid

Percolating water added to the soil by precipitation, irrigation, or waste applications may pass through the treatment zone and may rapidly transport some mobile waste constituents or degradation products through the unsaturated zone to the ground water. Soil-pore liquid monitoring is intended to detect these rapid pulses of contaminants (often immediately after heavy precipitation events) that are not likely to be observed through the regularly scheduled analysis of soil cores. Therefore, the timing of soil-pore liquid sampling is a key to the usefulness of this technique. Seasonability is the

rule with soil-pore liquid sample timing (i.e., scheduled sampling cannot be on a preset date, but must be geared to precipitation events). Given that sampling is done soon after leachate-generating precipitation or snowmelt, the frequency also varies depending on site conditions. As a starting point, sampling should be done quarterly. More frequent sampling may be necessary at units located in areas with highly permeable soils or high rainfall, or at which wastes are applied very frequently. The timing of sampling should be geared to the waste application schedule as much as possible.

At land treatment units where wastes are applied infrequently (i.e., only once or twice a year) or where leachate-generating precipitation is highly seasonal, quarterly sampling and analysis of soil-pore liquid may be unnecessary. Because soil-pore liquid sampling is instituted primarily to detect fast-moving hazardous constituents, monitoring for these constituents many months after waste application may be useless. If fast-moving hazardous constituents are to migrate out of the treatment zone, they will usually migrate within at least 90 days following waste application, unless little precipitation or snowmelt has occurred. Therefore, where wastes are applied infrequently or leachate generation is seasonal, soil-pore liquid may be monitored less frequently (semiannually or annually). A final note about timing is that samples should be obtained as soon as liquid is present. The owner or operator should check the monitoring devices for liquid within 24 hr of any significant rainfall, snowmelt, or waste application.

The background concentrations of hazardous constituents in the soil-pore liquid should be established by installing two monitoring devices at random locations for each soil series present in the treatment zone. Samples should be taken on at least a quarterly basis for at least one year and can be composited to give one sample per quarter. Analysis of these samples should be used to calculate an arithmetic mean and variance for each hazardous constituent. After background values are established, additional soil-pore liquid samples should occasionally be taken to determine if the background values are changing over time.

The number of soil-pore liquid samplers needed is a function of site factors that influence the variability of leachate quality. Active, uniform areas should receive, in the beginning, a minimum of six samplers per uniform area. For uniform areas >5 ha, at least two samplers per 1.5 ha (4 ac) should be installed. Samples may be composited in pairs based on location to give three samples for analysis. The number of devices may have to be adjusted up (or down) as a function of the variability of results.

To date, most leachate collection has been conducted by scientists and researchers, and there is not an abundance of available field equipment and techniques. The U.S. EPA (1977) and Wilson (1980) have prepared reviews of pressure vacuum lysimeters and trench lysimeters. The pressure vacuum lysimeters are much better adapted to field use and have been used to monitor pollution from various sources (Manbeck, 1975; Nassau-Suffolk Research Task Group, 1969; The Resources Agency of California, 1963; James, 1974). These pressure vacuum samplers are readily available commercially and are the most widely used, both for agricultural and waste monitoring uses. A third type of

leachate sampler is the vacuum extractor as used in the field by Smith et al. (1977). A comparison of in situ extractors was presented by Levin and Jackson (1977).

These soil-pore liquid sampling devices are described in Chapter Nine of this manual (in Part III, Sampling).

12.4.6 Treatment Zone Monitoring and Sampling Strategy

Treatment zone monitoring of land treatment units is needed for two purposes. One main purpose is to monitor the degradation rate of the organic fraction of the waste material and parameters significantly affecting waste treatment. Samples are needed at periodic intervals after application to be analyzed for residual waste or waste constituents. Such measurements need to be taken routinely, as specified by a soil scientist. These intervals may vary from weekly to semiannual, depending on the nature of the waste, climatic conditions, and application scheduling. The second major function of treatment zone sampling is to measure the rate of accumulation of conserved waste constituents to provide some indication of the facility's life.

The sampling schedule and number of samples to be collected may depend on management factors, but a schedule may be conveniently chosen to coincide with unsaturated zone soil core sampling. For systems that will be loaded heavily in a short period, more (and more frequent) samples may be needed to ensure that the waste is being applied uniformly and that the system is not being overloaded. About seven to ten samples from each selected 1.5-ha (4-ac) area should be taken to represent the treatment zone, and these should be composited to obtain a single sample for analysis. In addition, if there are evidently anomalous "hot spots," these should be sampled and analyzed separately.

12.4.7 Air Monitoring and Sampling Strategy

The need for air monitoring at a land treatment unit is not necessarily dictated only by the chemical characteristics of the waste. Wind dispersal of particulates can mobilize even the most immobile, nonvolatile hazardous constituents. Therefore, it is suggested that land treatment air emissions be monitored at frequent intervals to ensure the health and safety of workers and adjacent residents. This effort may be relaxed if the air emissions are positively identified as innocuous compounds or too low in concentration to have any effect. Although air monitoring is not currently required, it is strongly recommended because wind dispersal is a likely pathway for pollutant losses from a land treatment unit.

Sampling generally involves drawing air over a known surface area at a known flow rate for a specified time interval. Low-molecular-weight volatiles may be trapped by solid sorbents, such as Tenax-GC. The high-molecular-weight compounds may be sampled by Florisil, glass-fiber filters, or polyurethane foam.

12.5 ANALYSIS

12.5.1 Analytical Considerations

Parameters to be measured include pH, soil fertility, residual concentrations of degradable rate-limiting constituents (RLC), and the concentrations of residuals that limit the life of the disposal site (CLC), plus those that, if increased in concentration by 25%, would become limiting. Hazardous constituents of concern should also be monitored. Based on the data obtained, the facility management or design can be adjusted or actions taken, as needed, to maintain treatment efficiency. Projections regarding facility life can also be made and compared with original design projections. Because the treatment zone acts as an integrator of all effects, the data can be invaluable to the unit operator.

The analyst should use specific methods in this manual for determining hazardous waste constituents.

12.5.2 Response to Detection of Pollutant Migration

If significant concentrations of hazardous constituents (or PHCs) are observed below the treatment zone, the following modifications to unit operations should be considered to maximize treatment within the treatment zone:

1. Alter the waste characteristics.
2. Reduce waste application rate.
3. Alter the method or timing of waste applications.
4. Cease application of one or more particular wastes at the unit.
5. Revise cultivation or management practices.
6. Alter the characteristics of the treatment zone, particularly soil pH or organic matter content.

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CHAPTER THIRTEEN

INCINERATION

13.1 INTRODUCTION

Environmental Protection Agency regulations require owners or operators of hazardous waste incinerators to perform specific testing prior to issuance of a final permit. These regulations are contained in 40 CFR Parts 264.340-264.347, 270.19, and 270.62.

The regulations require that incinerated hazardous wastes be destroyed with an efficiency of 99.99% or higher. In order to obtain a permit to incinerate hazardous wastes, owners or operators must demonstrate that their incinerator can operate at the required efficiency (usually referred to as destruction and removal efficiency, or DRE). This demonstration will most often involve a "trial" burn. Prior to the trial burn, the owner or operator must test the hazardous waste being evaluated for incineration and determine the presence and concentration of Appendix VIII constituents, along with other parameters. The analytical results obtained will allow the owner or operator to determine the principal organic hazardous constituents (POHCs) in the waste. These POHCs will usually be those compounds in the waste that are difficult to burn, toxic, and found at reasonably high concentrations in the waste. During the trial burn, the POHCs are monitored to determine whether the incinerator is meeting the required DRE.

The owner or operator will then prepare an incineration permit application, which is submitted to the appropriate state and EPA region. Contents of permits are listed in Sections 270.14, 270.19, and 270.62 of the RCRA regulations. As part of the permit application, the owner or operator will provide the waste analysis information, propose certain POHCs for the trial burn, and specify the sampling and analysis methods that will be used to obtain the trial burn data. This portion of the permit application is called the "trial burn plan." The regulatory agency(ies) will review the application and trial burn plan, make any necessary modifications, and authorize the owner to conduct the trial burn. After the trial burn, the results are submitted to the permit issuance authority and, assuming all requirements are met, a final incineration permit will be issued. The permit contains all the information pertaining to the licensed operation of the incinerator, and the owner or operator must comply with whatever conditions are specified in the permit. The rest of this chapter will explain the various sampling and analysis strategies that can be used during the trial burn and how analysis data can be used to obtain a final permit.

13.2 REGULATORY DEFINITION

As explained earlier, incinerator regulations are contained in 40 CFR Parts 264.340-.347, 270.19, and 270.62. Because Part 264 contains general requirements for hazardous waste incineration, it will not be discussed here.

Parts 270.19 and 270.62 describe actual sampling and analysis requirements and are summarized below. A summary of the major analytical requirements is given in this section and is followed by sections detailing acceptable sampling and analysis methods for meeting these requirements.

The trial burn plan must include the following items:

1. Heat value of the waste.

2. Viscosity or physical description.

3. A list of hazardous organic constituents that are listed in Appendix VIII and that are reasonably expected to be present in the waste.

4. Approximate concentration of those compounds.

5. A detailed description of sampling and analysis procedures that will be used.

During the trial burn (or as soon after as possible), the following determinations must be made:

1. The concentration of trial POHCs in the waste feed.

2. The concentration of trial POHCs, mass emissions, oxygen, and hydrogen chloride in the stack gases. (Determination of the oxygen and water concentration in the stack exhaust gas concentration is necessary for correction of measured particulate.)

3. The concentration of trial POHCs in any scrubber water, ash, or other residues that may be present as a result of the trial burn.

4. A computation of the DRE.

For routine operation, the only explicit sampling and analysis requirement is the determination of carbon monoxide in the stack gas. Although the permit writer or the state/local authorities may impose additional monitoring requirements in some instances, it is not anticipated that comprehensive sampling of the stack-gas effluent or specific analysis of POHCs will be required, except in trial burn situations.

13.3 WASTE CHARACTERIZATION STRATEGY

13.3.1 Sampling

Acquisition of a representative sample of hazardous waste for subsequent chemical analysis is accomplished by preparing a composite of several subsamples of the waste. Sampling equipment and tactics for collection of the subsamples are specified in Chapter Nine of this manual and generally involve grab sampling of liter- or kilogram-sized portions of waste materials. To

ensure that the bulk of the waste is represented by the composite sample, the sampling strategy requires collection of a minimum of four subsamples that provide integration over both the depth and the surface area of the waste as contained in drums, tanks, holding ponds, etc. The composite sample prepared in the field must be mixed thoroughly and split into at least three replicate samples prior to shipment to the analytical laboratory. This step is primarily a precaution against breakage or loss of sample, but it also provides the potential for a check on the homogeneity of the composite sample. To ensure that sampling and analysis results will withstand legal scrutiny, chain-of-custody procedures are incorporated into sampling protocols. The sampling protocols also include explicit provisions for ensuring the safety of the personnel collecting the samples.

13.3.2 Analysis of Hazardous Wastes

The overall strategy for waste characterization includes test procedures (to determine the characteristics of the waste) and analysis procedures (to determine the composition of the waste). The analysis procedures can be divided into three sections:

1. Characteristics (useful for storage, etc.; not required).

2. Proximate analysis (useful data but not required, except for heat value).

3. Specific analysis (required for determination of POHCs).

Figure 13-1 provides an overview of this analytical approach. The discussion below provides a capsule description of each major element of this scheme and the use of the resulting information in the hazardous waste incineration permitting process.

13.3.2.1 Characteristics

The characteristics of the waste sample, defined in terms of ignitability, corrosivity, reactivity (including explosivity and toxic gas generation), and extraction procedure toxicity, are determined according to the procedures presented in Chapter Eight of this manual. These tests are performed on a sample from each waste stream, unless there is sufficient information from an engineering analysis to indicate the waste meets any of these criteria. This information is relevant to the Part 264, Subpart B, General Waste Analysis requirement in that it affects procedures for safely storing, handling, and disposing of the waste at the facility. The data are also relevant to possible exclusion from the trial burn requirements of Part 122. The data on the characteristics of each hazardous waste may be available from the waste generator and from manifest or shipping papers received by the facility owner/operator.

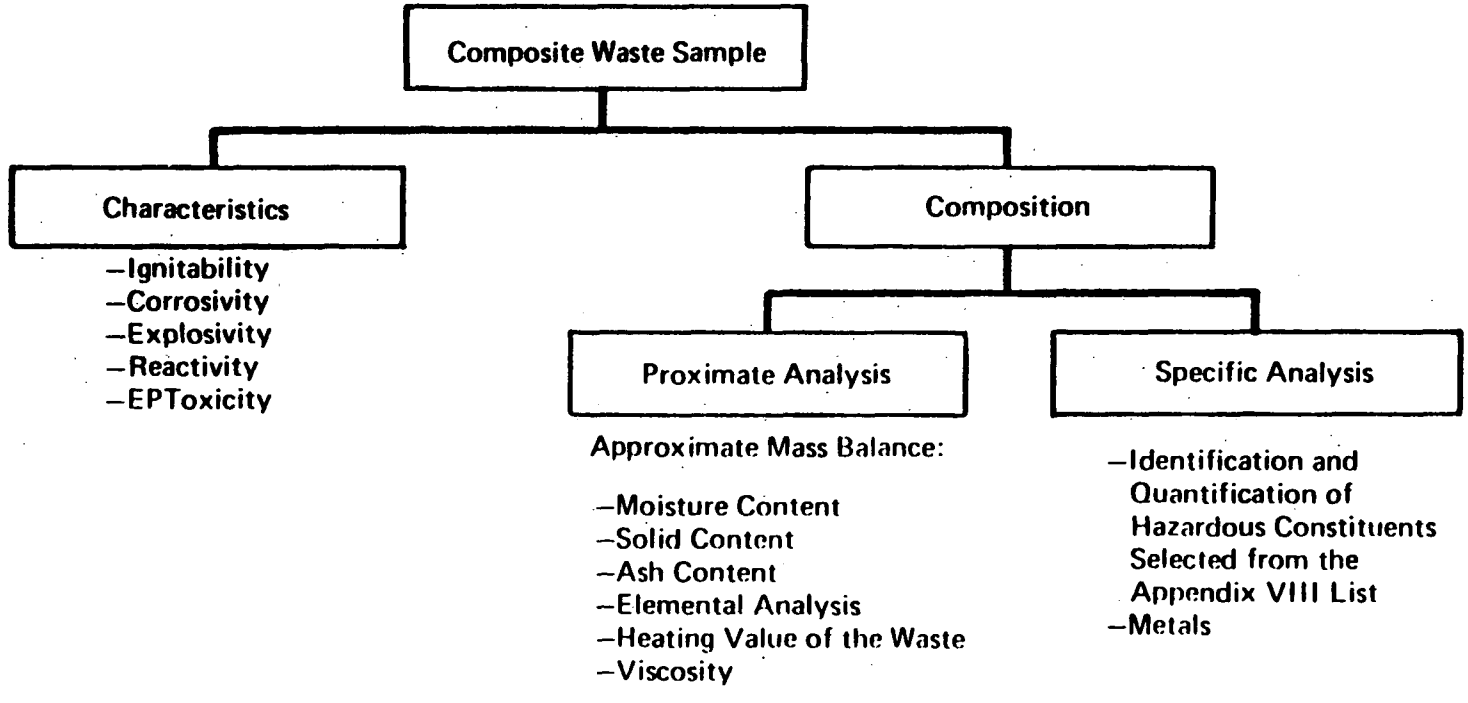


Figure 13-1 Overview of the analytical approach for waste characterization.

13.3.2.2 Proximate Analysis

The proximate analysis provides data relating to the physical form of the waste and an estimate of its total composition. This analysis includes determination of:

1. Moisture, solids, and ash content.

2. Elemental composition (carbon, nitrogen, sulfur, phosphorus, fluorine, chlorine, bromine, iodine to 0.1% level).

3. Heating value of the waste.

4. Viscosity.

Some or all of this information may satisfy the waste analysis requirements of the Part 264 regulations, as well as be responsive to the General Waste Analysis requirements of Subpart B. The elemental composition data allow one to predict if a high concentration of potentially significant combustion products (NO_x, SO_x, P_2O_5, hydrogen halides, and halogens) might be formed during incineration. These data also facilitate an informed selection of the Appendix VIII hazardous constituents that might be present in the waste by indicating whether the overall waste composition and hence the types of components present are consistent with expectations based on best professional judgment. For example, if bromine were not present in the waste, any organobromine compounds from Appendix VIII at levels of 1,000 mg/kg would be excluded from specific analysis.

13.3.2.3 Specific Analysis

The specific analysis portion of the waste characterization scheme provides qualitative confirmation of the presence and identity of the Appendix VIII constituents that might reasonably be expected to be present in the waste, based on professional judgment or on the results of proximate analysis. It is important to note that specific analysis does not involve screening every waste sample for all Appendix VIII hazardous components. A preliminary judgment is made as to the compounds or types of compounds that are actually present.

For the specific organic analyses, a high-resolution separation technique (fused-silica capillary gas chromatography) and a high-specificity detection technique (mass spectrometry) are used wherever possible. This approach ensures qualitative and quantitative analysis for a variety of waste types and process chemistries.

Specific analysis methods in this manual can be used for Appendix VIII constituents. Generally, the methods of choice for Appendix VIII components will be:

Method 6010	(Inductively Coupled Plasma Method)
Method 8270	(GC/MS Method for Semivolatile Organics: Capillary Column Technique)
Method 8240	(GC/MS Method for Volatile Organics)

Other more specific methods contained in this manual may be used; however, they cannot screen for a wide range of compounds. For example, Method 8010 can detect only those volatile compounds containing halogen.

13.3.3 Selection of POHCs

The criteria for selection of POHCs (typically one to six specific constituents per waste feed) include:

1. The expected difficulty of thermal degradation of the various hazardous organic constituents in the waste.

2. The concentration of those constituents in the waste.

It is anticipated that the designation of POHCs will be negotiated on a case-by-case basis for each permit application. It is important to note that it is not necessarily, or even generally, true that all Appendix VIII compounds present in the waste will be designated as POHCs. The intent is to select a few specific compounds as indicators of incinerator performance. The selected compounds should provide a sufficiently stringent test of the incinerator's performance to ensure that incineration of the waste can be carried out in an environmentally sound fashion. This criterion mandates selection of the more thermally stable constituents as POHCs.

At the same time, however, it is necessary that the designated POHCs be present in the waste in sufficiently high concentrations in order to be detected in the stack gas. This is a particularly important constraint for wastes that are to be incinerated with substantial quantities of auxiliary fuel, which effectively dilute the POHCs in the exhaust gas. Although the burning of auxiliary fuel might not affect the mass emission rate of POHCs, it would lead to an increased volumetric flow of stack gas and thus to a decreased concentration of POHCs at the stack. This lower concentration directly affects the detection limit achievable for a given stack-gas sample size (e.g., between 5 m^3 and 30 m^3).

It is recommended that, whenever possible, the permit writer select POHCs present in the waste at 1,000 mg/kg or higher. If it is considered desirable to designate as a POHC a thermally stable compound present at the hundreds-of-parts-per-million level, the trial burn permit application must include calculations and supporting data to indicate that 0.01% of the mass feed rate of that component in the waste could in fact be detected in the stack effluent. A waste concentration of 100 mg/kg probably represents a practical lower level below which determination of 99.99% DRE may require extraordinary

sampling analysis and quality control procedures, which may significantly increase the sampling and analysis costs for that trial burn.

For a waste material that is a listed hazardous waste under RCRA regulations (40 CFR Part 261, Subpart D), the constituents that caused the Administrator to list the waste as toxic (tabulated in Appendix VII of 40 CFR Part 261) would be logical candidates for designation as POHCs, if these constituents are organic chemicals.

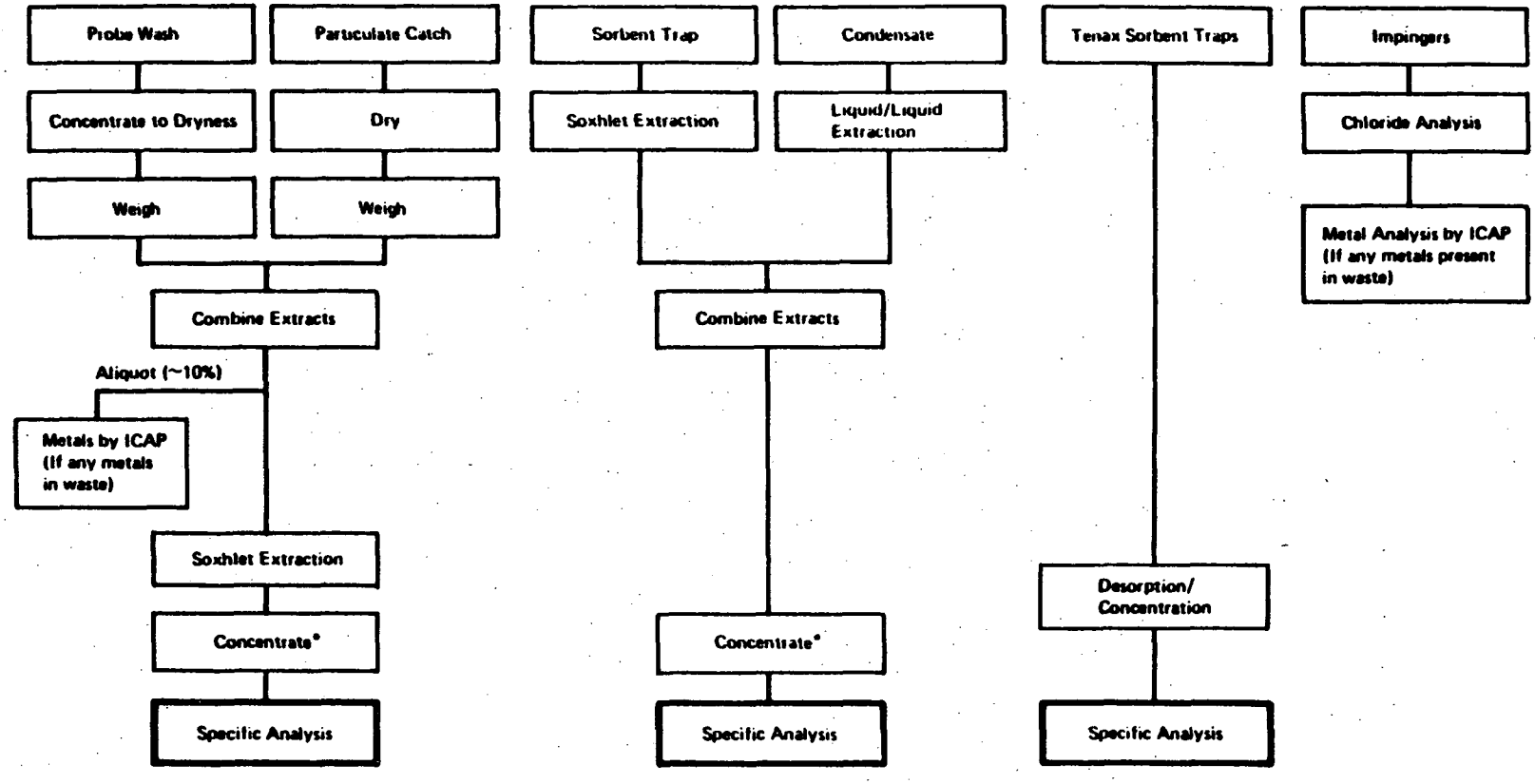
13.4 STACK-GAS EFFLUENT CHARACTERIZATION STRATEGY

The overall strategy for hazardous-waste-incinerator stack-gas effluent characterization to determine compliance with Part 264 performance standards is to collect replicate 3- to 6-hr, 5- to 30-m^3 samples of stack gas using a comprehensive sampling train, such as the EPA Modified Method 5 Sampling Train (MM5), the EPA/IERL-RTP Source Assessment Sampling System (SASS), or, for the volatile species, the Volatile Organic Sampling Train (VOST). These three strategies are described in detail in Chapter Ten (Methods 0010, 0020, and 0030). Any of the comprehensive sampling trains provides a sample sufficient for determination of particulate mass loading, concentrations of particulate and low-volatility vapor-phase organics, and concentrations of particulate and volatile metals. The VOST is used to collect the sample to be analyzed for volatile organic species. For burns of wastes that could also produce significant emissions of HCl, an MM5 type of train is used to collect and quantify HCl in the stack gas.

Figure 13-2 shows an overview of the analysis scheme for stack-gas samples. A separate sample (cyclone and particulate catch) will be used for determination of particulate mass loading and extraction of nonvolatile organic components. Heating during the particulate determination may drive off semivolatile organics. Volatile organic components of the stack gas will be collected using the VOST.

The directed analysis shown in Figure 13-2 is performed on triplicate samples. Although analysis of only two samples would allow an average level of a POHC to be determined, at least three samples should be analyzed so that an error bound for the measured values can be computed. The incremental cost of the replicate sampling and analysis is offset by increased confidence in the resulting data; quantitative results from a single sampling and analysis run should not generally be considered as an acceptable indicator of performance.

The survey analysis, which is a qualitative screen of the collected material to ensure that potentially hazardous but unexpected emissions do not go overlooked, need be performed on no more than one stack-gas sample. During a trial burn, the oxygen level in the stack gas must be measured using an Orsat or Fyrite analyzer, as detailed in 40 CFR Part 60, Appendix A, Method 3, so that the particulate loading may be corrected to a standard excess air level.



*As an alternative, the extracts from particulate and vapor portions of the train may be combined prior to analysis.

Figure 13-2 Overview of an analysis scheme for stack gas samples from a comprehensive sampling train.

For both trial and operating burns, on-line monitors (nondispersive infrared instruments) are used to provide continuous readings of carbon monoxide levels in the incinerator effluent.

13.5 ADDITIONAL EFFLUENT CHARACTERIZATION STRATEGY

The basic strategy for sampling scrubber water, ash, and other residue (if any) is to prepare composite samples from grab subsamples, collected using the same types of sampling devices and tactics as those used for waste characterization. This sampling is required only during trial burns, in accordance with 40 CFR Part 270.62. These additional effluent samples are analyzed for POHCs to determine appropriate disposal or subsequent treatment methods and to ensure that significant discharges of POHCs in other media do not go undetected.

13.6 SELECTION OF SPECIFIC SAMPLING AND ANALYSIS METHODS

The preceding discussion has briefly described the RCRA regulations that define sampling and analysis requirements for hazardous waste incineration and has presented an overview of the sampling and analysis procedures developed to meet these requirements.

This section will illustrate, by means of a hypothetical example, the transition from strategies, as described above, to methods, as described below. In the interest of clarity, the example is oversimplified, but should serve as a demonstration of how to develop and evaluate a hazardous waste incineration trial burn plan. The discussion will deal with sampling and analysis considerations only and will not address adequacy of design, operating conditions, or other engineering considerations.

13.6.1 Scenario

The owner/operator of an incineration facility seeks an RCRA permit to treat chlorinated organic waste material.

The facility is a liquid injection incinerator with a capacity of 10 x 10^6 Btu/hr and equipped with a wet scrubber for acid-gas removal. A waste oil (<0.1% chlorine) is burned as auxiliary fuel. The proposed operating conditions for hazardous waste incineration include a combustion zone temperature of 2000°F (1100°C) and a residence time of 2 sec with 150% excess air.

The waste is a still bottom from the production of perchloroethylene. Based on engineering analysis, it is expected to be a nonviscous organic liquid with a heating value >5,000 Btu/lb. The major components of the waste are expected to be highly chlorinated species such as hexachlorobenzene, hexachlorobutadiene, and other chlorinated aliphatic and aromatic compounds.

13.6.2 Strategy

There are insufficient data from other trial or operating burns to specify operating conditions under which this type of facility, when burning this type of waste, has been demonstrated to comply with the Part 264 performance criteria. Therefore, a trial burn will be required.

There are insufficient data to develop the trial burn plan available from the waste generator. Therefore, additional analyses of the waste will be necessary to support the trial burn permit application. The POHCs for which destruction and removal efficiencies are to be demonstrated in the trial burn must be designated, based on review of existing information and/or additional analysis of a representative sample of the waste.

Because the owner/operator plans to operate the facility under one set of temperature, residence time, and excess air conditions when treating hazardous waste, the trial burn will consist of three replicate tests under that set of operating conditions.

The trial burn sampling and analysis strategy must address:

1. The waste analysis requirements of 40 CFR Part 270.

2. The performance standards of 40 CFR Part 264, Subpart O.

3. The monitoring requirements of 40 CFR Part 264, Subpart O.

13.6.2.1 Sampling Strategy

During each of the three replicate tests, the following samples must be obtained:

1. One composite sample of the waste actually treated.

2. One time-averaged (3-4 hr) sample of stack gas.

3. One composite sample of spent scrubber water.

No bottom ash or fly ash streams (other than the stack particulate emissions) are expected to be generated as effluents from this facility.

13.6.2.2 Analysis Strategy

The waste must be analyzed to determine:

1. Quantity of designated trial burn POHCs.

2. Heating value of the waste.

3. Viscosity or physical form.

4. Quantity of organically bound chlorine. (This analysis is not mandatory; however, the data obtained may be helpful in determining a potential for HCl emissions.)

5. Identity and approximate quantity of known or suspected Appendix VIII constituents.

The stack gas must be analyzed to determine:

1. Quantity of designated trial burn POHCs.

2. Quantity of particulate matter emissions.

3. Quantity of hydrochloric acid emissions.

4. Carbon monoxide level.

5. Excess air level (oxygen/carbon dioxide level determination).

The scrubber water must be analyzed to determine quantities of designated trial burn POHCs.

13.6.3 Tactics and Methods

13.6.3.1 Selection of POHCs

The first step is to obtain a composite of the waste and to analyze it for Appendix VIII constituents. In this case the waste was sampled from a tank truck by taking a series of vertical cores at the available hatch location on the truck. The cores were obtained by using a Coliwasa (see Section 9.2.2.4 of Chapter Nine) and following the procedures. After the waste sample was collected, it was sent to the laboratory using chain-of-custody procedures (Section 9.2.2.7 of Chapter Nine) and was analyzed using Method 8270 (Chapter Four) (in this case the sample was directly injected with a split ratio of 100:1). The sample was also analyzed by Method 9020, Chapter Five. Table 13-1 summarizes the information that was obtained for the waste analysis. The major organic components that would appear to be candidates for selection as POHCs are listed in Table 13-2, along with relevant physical/chemical properties and recommended stack sampling and analysis methods.

The permit writer has designated hexachloro-butadiene, hexachlorobenzene, and hexachloroethane as POHCs. All three species are present in significant concentrations in the waste and will remain at >1,000 mg/kg concentration even if the waste were cut by as much as 1:10 with auxiliary fuel in order to limit the total chlorine feed rate and to maintain an adequate heating value in the total incinerator feed. Fully chlorinated species such as these are generally considered to be highly resistant to thermal degradation and thus provide an appropriate set of POHCs for DRE determination.

TABLE 13-1. INFORMATION ON COMPOSITION OF HYPOTHETICAL WASTE

Visual Inspection: The waste was a pitch-black, nonviscous liquid with obvious particulate loading. It had a pungent odor and fumed slightly when the cap was removed.

Loss on Ignition: Ignition at 900°C resulted in a 99.8% loss of mass.

Higher Heating Value: The waste would not burn in a bomb calorimeter; its higher heating value is estimated at approximately 2,000 Btu/lb.

TOX: 74.4% Cl.

GC/MS: This analysis indicates that hexachlorobutadiene is the major component (65%) and hexachlorobenzene is present at about 10% of the Total Organic Chlorine concentration. Other peaks in the chromatogram were identified as hexachloroethane (approx. 4%), tetrachloroethanes (approx. 3%), tetrachloroethylene (approx. 0.1%), plus four other chlorinated aliphatics at about 0.5% concentration of the CCl concentration.

Summary: All of the available evidence suggests that this waste contains essentially no perchloroethylene, that hexachlorobutadiene makes up about 65% of the waste, and that there are perhaps a dozen other components at 1-5% concentration. All of the minor components appear to be chlorinated, with hexachlorobenzene the most abundant.

TABLE 13-2

CANDIDATE POHCs FOR HYPOTHETICAL WASTE AND
RECOMMENDED STACK SAMPLING AND ANALYSIS METHODS
FOR HYPOTHETICAL TRIAL BURN

Compound (POHC)	Approx. concentration in waste (%)	B.P. (°C)	ΔH^a (kcal/mole)	MW (g/mole)	Stack Sampling Method		Analysis Method	
					Section number	Description	Method number	Description
Hexachlorobutadiene	65	215	N/A	260.76	1.2.1.8[b]	M5 - Sorbent	8120, 8250, or 8270	GC/MS Extractables
Hexachlorobenzene	6	323	567.7	284.8	1.2.1.8[b]	M5 - Particulate and Sorbents	8120, 8250, or 8270	GC/MS Extractables
Hexachloroethane	2	186.8	173.8	236.74	1.2.1.8[b]	M5 - Sorbent	8120, 8250, or 8270	GC/MS Extractables
Tetrachloroethane[c]	1.5	130.5 (146.2)	230 (233)	167.84	1.2.1.13	VOST	8010 or 8240	GC/MS Volatiles
Tetrachloroethylene	0.1	121.0	197	165.85	1.2.1.13	VOST	8010 or 8240	GC/MS Volatiles

[a]The standard enthalpy of combustion.

[b]The SASS method (Chapter Nine, Method 0020) could also be selected. A specially fabricated glass-lined SASS train might be necessary to withstand the hydrochloric acid expected in the stack.

[c]Numbers given in parentheses refer only to 1,1,2,2-tetrachloroethane.

13.6.3.2 Selection of Sampling Methods

For sampling of wastes and liquid and solid effluents, the choice of method is based primarily on the nature of the medium. Review of available methods indicates that for dipper sampling (Chapter Nine) or sampling from the tap of the waste-feed pipe would be appropriate for collection of discrete subsamples of waste feed and of spent scrubber water at regular time intervals over the duration of each trial burn. These would then be combined to form the corresponding composite samples for each test.

For sampling of stack gas, both the nature of the medium and the nature (volatility, stability) of the POHC or other target species affect the choice of a sampling method. Table 13-2 summarizes these recommendations for the candidate POHCs in this example. Note that designation of tetrachloroethylene as a POHC in this instance would require use of VOST, although the MM5 or SASS approaches would collect all of the other candidate POHCs.

The MM5 train would also suffice to determine compliance with the two other performance standards of 40 CFR Part 264. The particulate matter emission rate can be determined from the mass of material collected in the probe wash, cyclone (if any), and filter of the MM5 train. The hydrochloric acid emission rate can be determined by using caustic scrubbing solution in the impinger portion of the MM5 train and determining the hydrochloric acid level as chloride.

In addition to the procedures chosen for the collection of POHCs, it would be necessary to specify procedures for the required monitoring for carbon monoxide and oxygen levels in the stack gas.

13.6.3.3 Selection of Analysis Methods

The analytical procedures used for qualitative identification and quantitative determination of POHCs and other target species are determined primarily by the nature (volatility, polarity) of the species sought.

This manual lists recommended analysis methods for each candidate POHC after the appropriate sample preparation steps in Methods 0010, 0020, and 0030 have been performed. Table 13-2 summarizes the recommendation for analysis of the candidate POHCs in this hypothetical example. Note that a single analytical method suffices to determine all of the hexachlorospecies of concern here although an additional method would be recommended if the analysis were to include the tetrachloroethanes and tetrachloroethylene.

13.6.4 Results and Calculations

This section illustrates the proper methods for calculating DRE, corrected particulate loading, and HCl emissions for the hypothetical example described above. Again, this example has been somewhat oversimplified for purposes of illustration.

According to 40 CFR Part 264, the DRE for each POHC is calculated as:

$$DRE = \frac{W_{in} - W_{out}}{W_{in}} \times 100\%$$

where:

W_{in} = mass feed rate of one POHC in the waste stream feeding the incinerator.

W_{out} = mass emission rate of the same POHC present in stack exhaust emissions.

13.6.4.1 Calculation of W_{in} (lb/hr):

$$W_{in} = \frac{C_W \times FR_W}{100}$$

where:

C_W = Concentration of one POHC in the waste, %.

FR_W = Mass feed rate of waste to the incinerator, lb/hr.

Assume that quantitative analysis of a representative aliquot drawn from the composite waste sample from test No. 1 gave the following concentrations:

hexachlorobutadiene	63 %
hexachlorobenzene	9.4%
hexachloroethane	1.1%

Further, assume that the thermal capacity of the facility (10×10^6 Btu/hr) was met by blending waste 1:10 with waste oil to give a feed mixture that was 8.2% chlorine and that had a heating value of 16,400 Btu/lb. The total mass feed rate to the incinerator was therefore 600 lb/hr, of which 540 lb/hr was auxiliary fuel (waste oil) and 60 lb/hr was chlorinated waste.

The W_{in} values for the three POHCs are therefore:

hexachlorobutadiene	(.63 x 60 lb/hr)	38 lb/hr
hexachlorobenzene	(.094 x 60 lb/hr)	5.6 lb/hr
hexachloroethane	(.011 x 60 lb/hr)	0.66 lb/hr

13.6.4.2 Calculation of W_{out} (lb/hr):

$$W_{out} = C_S \times ER_S \times 1.32 \times 10^{-4}$$

where:

C_S = Concentration of one POHC in the stack gas effluent, mg/dNm^3.

ER_S = Volumetric flow rate of stack gas, dNm^3/min.

1.32×10^{-4} = Conversion factor from mg/min to lb/hr.

Assume that quantitative analysis of the extract prepared from the time-integrated comprehensive sampling train sample from test No. 1 gave the following concentrations in the sampled gas:

hexachlorobutadiene	0.080 mg/m^3
hexachlorobenzene	0.020 mg/m^3
hexachloroethane	$\leq$0.004 mg/m^3

Further, assume that the average measured volumetric flow of stack gas during test No. 1 was 3,200 scfm or 90 dNm^3/min.

The W_{out} values for the three POHCs are therefore:

hexachlorobutadiene	$(.080 \times 90 \times 1.32 \times 10^{-4})$	9.5×10^{-4} lb/hr
hexachlorobenzene	$(.020 \times 90 \times 1.32 \times 10^{-4})$	2.4×10^{-4} lb/hr
hexachloroethane	$(\leq 0.004 \times 90 \times 1.32 \times 10^{-4})$	$< 0.48 \times 10^{-4}$ lb/hr

13.6.4.3 Calculation of DRE:

$$DRE = \frac{W_{in} - W_{out}}{W_{in}} \times 100$$

The DRE values for the three POHCs are therefore:

hexachlorobutadiene	99.997
hexachlorobenzene	99.996
hexachloroethane	>99.993

Note that compliance with a "four-9's" performance standard could not have been demonstrated in this particular example for a component present at <1% in the waste itself (or <1,000 mg/kg in the 1:10 waste:fuel blend fed to

the incinerator) unless the detection limit for that component in the stack gas were <4 ug/m^3.

In this example, compliance with the 99.99% DRE performance standard has been demonstrated, in one test, for each of the three POHCs. If these results were supported by data from the other two replicate trial burn tests, the "four-9's" DRE could be considered to have been established.

13.6.4.4 Calculation of HCl Emissions

An incinerator burning highly chlorinated hazardous waste capable of producing significant stack-gas emissions of hydrogen chloride (HCl) must monitor and/or control HCl emissions.

The hypothetical waste in this example contains approximately 75% chlorine by weight (Table 13-1). At the proposed 60-lb/hr feed rate of waste that is blended 1:10 with auxiliary fuel for a total feed of 600 lb/hr (9.8 x 10^6 Btu/hr), the maximum HCl emission rate would be 45 lb/hr of chlorine basis or 46 lb/hr as HCl. This rate exceeds the regulatory limit of 4 lb/hr; therefore, the scrubber efficiency must be determined.

The stack emission rate of HCl can be calculated from measured values in the following manner:

$$HCl_{out} = C_{in} \times ER_s \times 1.32 \times 10^{-4}$$

where:

C_{in} = Concentration of HCl in the stack-gas sample (mg/m^3).

ER_s = Volumetric flow rate of the stack gas, m^3/min.

1.32×10^{-4} = Conversion factor from mg/min to lb/hr.

Assume that quantitative analysis of the impinger/condensate solution from the time-integrated comprehensive sampling train from test No. 1 gave 34 mg/m^3 HCl in the stack effluent.

The stack emission rate of HCl is calculated by:

$$HCl_{out} = 34 \text{ mg/m}^3 \ (90 \text{ m}^3\text{/min}) \ (1.32 \times 10^{-4})$$

$$= 0.40 \text{ lb/hr HCl.}$$

This emission level is <1% of the 46 lb/hr of HCl potentially generated from the waste, an indication that the removal efficiency of the wet scrubber was >99%.

13.6.4.5 Calculation of Particulate Loading (mg/m^3)

An incinerator-burning hazardous waste must not emit particulate matter in excess of 180 mg/dscm when corrected to an oxygen concentration of 7% in the stack gas.

Assume that prior to chemical analysis, particulate samples from the stack effluent of the hypothetical waste (from probe washes and filter catches of the time-integrated comprehensive sample train) were dried and weighed. The hypothetical particulate loading from these measurements was calculated to be 80 mg/m^3 at the actual excess air level of the stack. The excess air level was determined to be 150%, based on hypothetical measured values of oxygen (12.8%) and carbon dioxide (6.7%). Correction to standard excess air level, as specified in the Part 264 regulations, leads to a particulate loading of 140 mg/m^3 (0.06 gr/scf). This total particulate emission is in compliance with the Part 264 performance standard that specifies $\leq$180 mg/m^3 ($\leq$0.08 gr/scf).

13.6.5 Summary

Incinerator performance in this example complies with the Part 264 Subpart O Incinerator Standards as they relate to:

1. Destruction and Removal Efficiency. All three POHCs showed compliance with the 99.99% DRE performance standard.

2. Limitation on HCl Emissions. The HCl emission rate of 0.40 lb/hr shows compliance with a 99% removal standard for HCl.

3. Limitation on Stack Emissions of Particulate Material. The corrected particulate loading of 140 mg/m^3 is less than the 180 mg/m^3 standard for particulate loading (corrected to a standard excess air level).

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APPENDIX

COMPANY REFERENCES

The following listing of frequently-used addresses is provided for the convenience of users of this manual. No endorsement is intended or implied.

Ace Glass Company
1342 N.W. Boulevard
P.O. Box 688
Vineland, NJ 08360
(609) 692-3333

Aldrich Chemical Company
Department T
P.O. Box 355
Milwaukee, WI 53201

Alpha Products
5570 - T W. 70th Place
Chicago, IL 60638
(312) 586-9810

Barneby and Cheney Company
E. 8th Avenue and N. Cassidy Street
P.O. Box 2526
Columbus, OH 43219
(614) 258-9501

Bio - Rad Laboratories
2200 Wright Avenue
Richmond, CA 94804
(415) 234-4130

Burdick & Jackson Lab Inc.
1953 S. Harvey Street
Muskegon, MO 49442

Calgon Corporation
P.O. Box 717
Pittsburgh, PA 15230
(412) 777-8000

Conostan Division
Conoco Speciality Products, Inc.
P.O. Box 1267
Ponca City, OK 74601
(405) 767-3456

Corning Glass Works
Houghton Park
Corning, NY 14830
(315) 974-9000

Dohrmann, Division of Xertex Corporation
3240 - T Scott Boulevard
Santa Clara, CA 95050
(408) 727-6000
(800) 538-7708

E. M. Laboratories, Inc.
500 Executive Boulevard
Elmsford, NY 10523

Fisher Scientific Co.
203 Fisher Building
Pittsburgh, PA 15219
(412) 562-8300

General Electric Corporation
3135 Easton Turnpike
Fairfield, CT 06431
(203) 373-2211

Graham Manufactory Co., Inc.
20 Florence Avenue
Batavia, NY 14020
(716) 343-2216

Hamilton Industries
1316 18th Street
Two Rivers, WI 54241
(414) 793-1121

ICN Life Sciences Group
3300 Hyland Avenue
Costa Mesa, CA 92626

Johns - Manville Corporation
P.O. Box 5108
Denver, CO 80217

Kontes Glass Company
8000 Spruce Street
Vineland, NJ 08360

Millipore Corporation
80 Ashby Road
Bedford, MA 01730
(617) 275-9200
(800) 225-1380

National Bureau of Standards
U.S. Department of Commerce
Washington, DC 20234
(202) 921-1000

Pierce Chemical Company
Box 117
Rockford, IL 61105
(815) 968-0747

Scientific Glass and Instrument, Inc.
7246 - T Wynnwood
P.O. Box 6
Houston, TX 77001
(713) 868-1481

Scientific Products Company
1430 Waukegon Road
McGaw Park, IL 60085
(312) 689-8410

Spex Industries
3880 - T and Park Avenue
Edison, NJ 08820

Waters Associates
34 - T Maple Street
Milford, MA 01757
(617) 478-2000
(800) 252-4752

Whatman Laboratory Products, Inc.
Clifton, NJ 07015
(201) 773-5800

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